SORPTION AND IDENTIFICATION OF $DIQUAT^{2+}$ AND $PARAQUAT^{2+}$ BY CLAY MINERALS

By

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CHAPTER I

INTRODUCTION

The sorption of organic compounds by clay minerals is dependent upon the chemical properties of the compounds and the type of clay minerals involved. Organic compounds paraquat (1, 1′ - dimethyl - 4, 4′ bipyridinum dichloride) and diquat (6, 7′ - dihydrodipyrido - (1, 2a:2′, 1′ - c) - pyrazidiinium dibromide) are soluble organic herbicides that ionize in water to form divalent organic cations. These compounds form free radicals by the uptake of one electron as the mode of herbical activity.

Two characteristics of paraquat and diquat are their deactivation by sorption in soil and their stability in soil. Since paraquat and diquat are stable in soil, these compounds are tightly sorbed by the soil cation exchange complex. The objective of this study was to determine the mode of sorption and geometry of interlayers of paraquat and diquat on clay minerals.

CHAPTER II

LITERATURE REVIEW

Paraquat, 1, 1′ - dimethyl - 4, 4′ - bipyridinium dichloride and diquat, 6, 7 - dihydrodipyrido - (1, 2a:2′, 1′ - c) - pyrazidinium dibromide were first reported by Brian et al. (5) in 1955. Since that time, many investigators have studied the fate of these herbicides in soils.

Harris and Warren (10) offered one of the first reports on the sorption of diquat on bentonite (calcium saturated), an organic soil, an anion-exchange resin, and a cation-exchange resin. They reported that diquat was completely sorbed by the bentonite, the cation exchanger, and strongly sorbed by the organic soil. On the other hand, the anion exchanger sorbed a constant amount at all diquat concentrations. Diquat displaced potassium ions from an organic soil whose exchange complex was saturated with potassium. The diquat acted as a cation in the soil and removal from solution appeared to be by an ion exchange mechanism.

Coats et al. (6) reported on the sorption of paraquat in soil and by clay minerals. A sandy loam soil with a C. E. C. of 2. 50 meq. /100g. apparently sorbed between 0. 2 and 0. 5 mg/g. of paraquat. Kaolinite sorbed between 2. 5 and 3. 0 mg/g. whereas montmorillonite sorbed between 75 and 85 mg/g. No cation-exchange capacities were given for the two clay minerals.

Weber et al. (21) and Weber and Scott (20) examined the influence of temperature and time on the sorption of diquat and paraquat on kaolinite, montmorillonite and charcoal. They found that paraquat and diquat were strongly sorbed on montmorillonite and kaolinite clays. Both compounds were found to be bound within the interlayer spacings of the montmorillonite clay by coulombic (ion exchange) and Van der Waals forces and to the surface of particles of kaolinite by coulombic ion exchange forces only. Both herbicides were sorbed by the clays to approximately the cation exchange capacity of the clay minerals. No herbicide was sorbed by the clays beyond this critical capacity and temperature had no effect on the total amount of the two organic cations sorbed or on the solubility. Diquat and paraquat were the least sorbed by charcoal, but the sorption was influenced by temperature and length of exposure time.

Desorption investigations indicate that about 80% of the sorbed cations on kaolinite could be removed with 1M $BaCl_2$. This contrasts with sorption on montmorillonite where only 5% could be removed. This probably indicates that the cations sorbed on the edges of the kaolinite clay particles are not held as strongly as those bound by montmorillonite. Possibly only coulombic forces are responsible for sorption on kaolinite, whereas additional physical forces are acting in the montmorillonite system. Considerable research has been performed on the interaction of organic compounds with clay minerals, especially montmorillonite, because of its expanding structure and high cation exchange capacity. The sorption of organic molecules by montmorillonite clay involves the entry of the organic molecules between the silicate sheets of clay, causing an expansion of the crystalline structure.

Weber et al. (21) have shown by x-ray analysis that diquat and paraquat are held in the structure of montmorillonite with the plane of the ring parallel to the silicate sheet.

Hendricks et al. (11) showed that the value of d(001) depends upon the structure of the organic cation and the manner in which it is sorbed onto the silicate surface. This dependence may be useful as a method for the determination of "molecular thickness" for Van der Waals adsorption. Knight and Tomlinson (14) examined the interaction of paraquat with eight mineral soils at 20° ± 2° C with 24 hours of contact. Langmuir adsorption isotherms were described where saturation uptake was less than the normal C. E. C. Typical quantities of sorbed paraquat (meq. /100g.) were: (a) sandy loam (C. E. C. = 2.88 meq. /100g.), 2.02; (b) loam (C. E. C. = 13.8), 9.8; and (c) clay (C. E. C. = 33.7), 25.7. Treatment with hydrogen peroxide eliminated most of the organic matter in the soil with a subsequent decrease in the C. E. C. and loss of capacity to sorb paraquat. Montmorillonite (C. E. C. = 80) and kaolinite (C. E. C. = 5.2) were equilibrated also with paraquat solutions with an uptake of 78.0 and 4.0 meq. /100g., respectively. The strong sorption capacity ("a region of the adsorption isotherm in which no paraquat could be detected in solution") of the eight soils was associated with the clay mineral fraction.

Tucker et al. (17) investigated the bonding of diquat and paraquat. This bonding was arbitrarily defined as: "loosely bound-eluted with saturated ammonium chloride," and "tightly bound-extracted by refluxing with 18N sulfuric acid." An "unbound" herbicide was eluted with water. In general terms, at low concentrations, paraquat or diquat desorption requires refluxing with 18N sulfuric acid. As the concentra-

tion of the herbicide in the soil increases, a portion of the paraquat or diquat can be desorbed by leaching with saturated ammonium chloride. At high saturation levels, some of the paraquat or diquat is unbound and can be leached with water. A particular soil has a definite capacity for each of the two types of sorbed paraquat or diquat and the capacities vary greatly with soil type.

Weber and Coble (19) researched the microbial decomposition of C^{14}-diquat sorbed on montmorillonite and kaolinite. Soil microorganisms were adapted to grow on diquat as a carbon source in an aerobic system. $C^{14}O_2$ release was inhibited completely in the montmorillonite system when the appropriate quantity of clay was present, i. e., when the C. E. C. was satisfied with diquat. On the other hand, sorption of the C^{14}-diquat on kaolinite did not inhibit $C^{14}O_2$ evolution. Weber and Coble believed that the difference between the two clay systems could be ascribed to the sorption of diquat into the structure of montmorillonite and therefore not available to microorganisms, even though several investigators have shown that the dipyridylium herbicides can be microbiologically degraded (3).

Weber et al. (22) and Weber and Weed (24) reexamined the question of adsorption and desorption of diquat and paraquat on and from Darco G-60 charcoal, exchange resins and by montmorillonite and kaolinite clay minerals. The Freundlich equation described the charcoal systems. At equilibrium concentrations of 5×10^{-6} M, the amount of diquat and paraquat sorbed were approximately 5.0 and 7.0μ mole/g. of charcoal, respectively. The desorption isotherms (deionized water extractions) essentially fell on the adsorption isotherms which suggests equilibria were attained in each system. Diquat and paraquat were

sorbed by the cation exchange resins (H and Na^+ forms) and both herbicides were readily desorbed by Na^+ ions but not with deionized water. Diquat was preferentially sorbed over paraquat by the cation exchange resins and diquat was also effective in displacing paraquat from the resins. In the case of montmorillonite and kaolinite clays, however, diquat and paraquat were sorbed to approximately the cation exchange capacity of the clays. Approximately 80% of each of the herbicides was displaced from kaolinite clay with Ba^{2+} ions. A total of 5% of each of the compounds was removed from montmorillonite with 1M $BaC\ell_2$ solutions. The two herbicides were found to exchange for one another on both clay minerals in a one-for-one manner. Paraquat was preferentially sorbed over diquat by both clays in competitive ion studies and was also found to be the more difficult of the two herbicides to displace.

Weed and Weber (25) studied the effect of adsorbent charge on the competitive sorption of divalent organic cations by layer-silicate minerals, and they found that paraquat was preferentially sorbed on all montmorillonites and on the external surface of vermiculite, whereas diquat was preferentially sorbed on the internal surface of vermiculite and on the external surface of nonexpanded mica. Grim (9) reported that organic cations such as the alkylamine take up exchange sites, on beidellites from various sources, in the interlayers of these expanding clays and will expand the structure to the full length of the alkyl chains.

Weed and Weber (26) and Weber and Weed (23) repeated their studies for sorption and desorption of paraquat and diquat. They found that diquat and paraquat were sorbed by montmorillonite, bentonite and various vermiculites in amounts equal to or less than the C.E.C. of the clays. The herbicides were sorbed by the montmorillonite and Utah

bentonite until the C. E. C. was entirely satisfied with little effect from the sorbed inorganic cations. Additions of various salt solutions released no more than 10% of the herbicide from the bentonite. The greatest percentage was released by $A\ell\ C\ell_3$ and this release was believed to be that which was sorbed on the external surfaces. They later showed that N-(4-pyridyl) - pyridinium chloride, a new phytotoxic organic cation was effective in desorbing the cationic herbicide diquat from montmorillonite for adsorption by cucumber seedlings. The reaction for the release of diquat is shown below:

$$\text{Diquat - clay} + 2\text{PPC}\ell^{+} \longrightarrow 2\text{PPC}\ell\text{ - clay} + \text{diquat}^{2+}.$$

Weber et al. (18) showed that the energies of sorption of diquat and paraquat are sufficiently great to more or less completely replace Na^{+}, Ca^{++} or Mg^{++} held on external or "open" sites, even at quite low concentrations of the herbicides. The availability of the herbicides, when sorbed on Ca^{++} montmorillonite, to cucumber seedlings was 5-10% which was probably that part sorbed on the external sites.

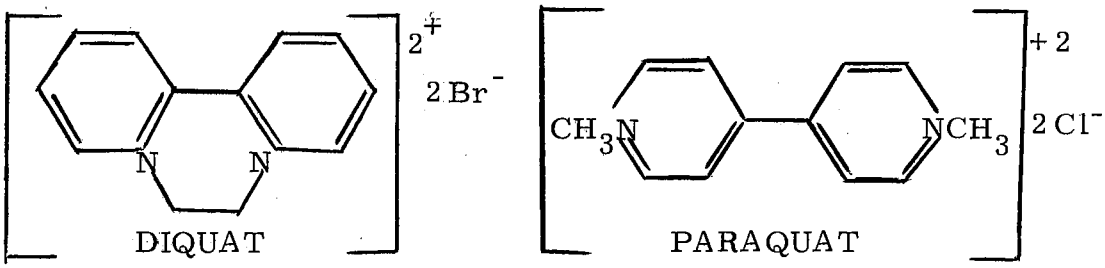
Dixon and Moore (7) found that the exchange of diquat in soil clays, vermiculite and smectite was replaced by washing samples with 1N$KC\ell$ solutions.. Exchange of diquat by K^{+} was 23% to 26% complete for three Wyoming montmorillonites and was 35% to 44% complete for three montmorillonite samples from Alabama and Mississippi. Diquat cations were 59% exchangable from a nontronite clay. The diquat cation satisfied 57% and 82% of the cation exchange charge of Texas and Montana vermiculite and K^{+} replaced 98% and 88% of the diquat, respectively. There was a direct relationship between K^{+} diquat exchange and layer charge density (C. E. C.) of the montmorillonite and vermiculite.

Hydroxy-Aℓ interlayers had little influence on the exchange of diquat on vermiculite and on montmorillonite except where double interlayers were deposited.

CHAPTER III

MATERIALS AND METHODS

Analytical grade diquat and paraquat were obtained from the California Chemical Company. The chemical structure of the compounds used are as follows:



Both diquat and paraquat ionize completely in aqueous solution to form the organic cation as shown in Table I:

TABLE I

PROPERTIES OF HERBICIDES USED IN SORPTION STUDIES

Common	Molecular	Solubility in H_{20}	Pk	Theoretical Parachor
Diquat	344.1	70%	Completely ionized	445.3 (cation)
Paraquat	257.2	100%	Completely ionized	473.4 (cation)

Sorbents selected for study are shown in Table II. The fine, coarse and very coarse fractions of the montmorillonite, illite and kaolinite clays were separated with the super centrifuge and saturated with Mg^{++} according to Jackson (13). The cation exchange capacities were determined by washing the clays four times with 1N $CaC\ell_2$. The excess salt was removed by washing the clays four times with deionized water and one time with 95% ethanol until the excess $CaC\ell_2$ was removed, as indicated by a negative $AgNO_3$ test for $C\ell$ in the last of the washings. Finally, the Ca is replaced by means of four washings with 1N $NaC\ell_2$. The extract solution was then brought to the volume with distilled water and the Ca content was measured by versene titration.

Ca Determination

Twenty-five mℓ aliquots from each sample were transferred into 100 mℓ beakers. Next, ten mℓ of the $NH_4C\ell$ - NH_4OH buffer solution was added to bring the solution to pH 10 and then ten drops of Eriochrome black T indicator solution and one mℓ of 2% NaCN solution were added. The solution titrated with .01 N versene solution to ice blue color endpoint. The C.E.C. were calculated as

$$\text{M.e./100g.m.} = \text{m}\ell \text{ versene x N x } \frac{100}{\text{sample weight in gm}} \quad (12).$$

Herbicide Determination

Paraquat and diquat solution were prepared in Na acetate buffer (pH 4.05) to give 2.572 and 3.441 mg/mℓ (0.02 N) of organic cation, respectively.

The standard curves were prepared according to directions from the Herbicide Handbook of the Weed Society of America (1), and are

indicated as follows:

1. One mℓ of 0,02 N paraquat and diquat were placed in a 500 mℓ volumetric flask and brought to volume with the buffer (pH 4.05), to give .005 mg/mℓ of paraquat and diquat cation. This was called solution A.

2. Solution B was made up to equal 0.004 mg/mℓ of paraquat and diquat cation.

3. Solution C was made up to equal 0.003 mg/mℓ of paraquat and diquat cation.

4. Solution D was made up to equal 0.002 mg/mℓ of paraquat and diquat cation.

5. Solution E was made up to equal 0.001 mg/mℓ of paraquat and diquat cation.

The sorbence of the solutions were determined with a Perkin-Elmer Model 202 ultra-violet visible spectrophotometer with the buffer solution as a reference. The standard curve peaks were obtained at 257 and 310 mu for paraquat and diquat, respectively.

Then portions of the stock solution of paraquat and diquat were added to the clay suspensions to give fully saturated, 3/4, 1/2, 1/4, 1/7 and 1/10 clay saturated exchange sites based on the previously determined C.E.C. value. The mixtures were then shaken for one hour and then centrifuged to give clear supernatant solutions.

An aliquot was taken from the supernatant paraquat and diquat saturated samples and quantity of herbicide determined on the spectrophotometer at 257 mu and 310 um (um = micrometers).

The clay samples were then mounted on microglass slides and the x-ray diffraction pattern developed. Later an attempt was made to determine the Aℓ -interlayer of clay samples, according to McLean (15).

CHAPTER IV

RESULTS AND DISCUSSION

The cation exchange capacity of the clay minerals are reported in Table II. The C.E.C. was determined by Ca^{++} replacement with Na^{+} and titration with EDTA. The C.E.C. obtained by saturation with paraquat and diquat are shown in Tables III through XIV and in Figures 1 through 12. The sorption of paraquat and diquat is depicted according to the following exchange reaction (21):

$$(\text{organic cation})^{2+} + (2\ \text{Mg - clay}) \rightleftarrows (\text{organic cation - clay}) + 2(\text{Mg}^{+}).$$

The reaction goes completely to the right until the C.E.C. of the clay is approached.

The following data sets forth the sorption rates of paraquat and diquat by clay minerals:

1. Sorption of diquat and paraquat by attapulgite. Diquat and paraquat were sorbed by attapulgite in amounts less than the C.E.C. (Table III). Diquat sorption exceeds paraquat sorption, probably due to the smaller size of diquat ion, which results in less steric hindrance (Figure 1). The fine fractions of attapulgite did not sorb as much paraquat and diquat as the coarse fraction sorbed.

2. Sorption of diquat and paraquat by montmorillonite clays. The montmorillonite clay minerals have a high cation exchange capacity (Table II). These minerals have a great sorption capacity due to high internal charge deficits (Tables IV through X). McAtee (16) showed

that exchange cations on hectorite are somewhat easier to replace with organic cations than those held on a Wyoming bentonite. He explained that in hectorite the charge on the structure is a consequence of replacements within the octahedral part of the structure only, whereas in Wyoming bentonite there are replacements in both the octahedral and tetrahedral parts of the structure. However, this was not the case in this study. The order of sorption of paraquat and diquat by montmorillonite clay groups was Belle Fourche montmorillonite > nontronite > Arizona bentonite > Wyoming bentonite > nontronite 35A or 33A > hectorite > beidellite. Diquat sorption exceeds paraquat sorption by montmorillonites probably due to the smaller size of the diquat ions, which results in less steric hindrance (Figures 2 through 8).

The fine fractions of the montmorillonite groups did not sorb as much paraquat and diquat as were sorbed by the coarse fractions. The organic cations were probably sorbed within the clay structure, since the predominance of exchange sites occur internally in montmorillonite clays.

3. Sorption of diquat and paraquat by vermiculite. The vermiculite clay has a high cation exchange capacity and, therefore, has a great capacity for sorption of diquat and paraquat (Table XI). Diquat sorption exceeds paraquat sorption by vermiculite probably due to the smaller size of the diquat ions (Figure 9).

The fine fractions of vermiculite did not sorb as much paraquat and diquat as the coarse fractions. The organic cations were probably sorbed within the clay structure.

4. Sorption of diquat and paraquat by Fithian illite. The sorption of paraquat and diquat by Fithian illite approaches the C.E.C. of the

TABLE II

CATION EXCHANGE CAPACITY OF CLAY MINERALS

	M. e./100g.		
Clay Minerals	2μ<	2-.2μ	<0.2μ
Attapulgite	26.52	27.94	84.55
Beidellite	--	55.03	65.91
Arizona Bentonite	113.42	100.53	104.83
Wyoming Bentonite	23.76	96.16	91.13
Belle Fourche Montmorillonite	--	76.53	73.98
Hectorite	79.93	--	118.34
Nontronite	82.52	83.66	75.50
Nontronite 35A or 33A	94.02	89.86	84.24
Vermiculite	101.74	113.58	101.26
Fithian Illite	8.77	9.97	91.74
Georgia Kaolinite	5.87	13.67	63.71
Stillwater Volcanic Ash	4.86	26.86	57.39

TABLE III

SORPTION OF DIQUAT AND PARAQUAT BY ATTAPULGITE (M. e./100g. OF C. E. C.)

% Saturation	Attapulgite					
	Diquat			Paraquat		
	> 2μ	2-. 2μ	<. 2μ	> 2μ	2-. 2μ	<. 2μ
Full	25.83	27.44	83.11	25.49	27.57	82.63
3/4	19.23	20.82	62.01	19.05	20.44	61.32
1/2	13.19	13.84	40.67	12.99	13.81	40.37
1/4	6.61	6.86	20.72	6.42	6.82	20.44
1/7	3.77	3.88	11.92	3.73	3.78	11.69
1/10	2.63	2.78	8.06	2.62	2.73	8.06

TABLE IV

SORPTION OF DIQUAT AND PARAQUAT BY BEIDELLITE (M.e./100g. OF C.E.C.)

% Saturation	Beidellite			
	Diquat		Paraquat	
	$>2\mu$	$<.2\mu$	$>2\mu$	$<.2\mu$
Full	53.77	64.04	53.41	63.47
3/4	40.48	47.92	40.25	47.46
1/2	27.38	32.77	27.37	32.74
1/4	13.69	16.32	13.68	16.28
1/7	7.97	9.36	7.96	9.33
1/10	5.42	6.48	5.40	6.46

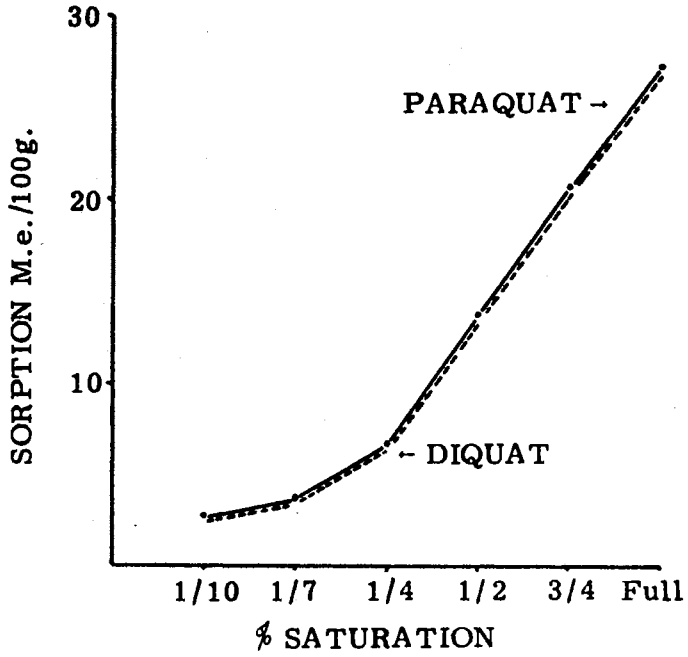


Figure 1. Sorption of Paraquat and Diquat by Attapulgite (2-.2μ)

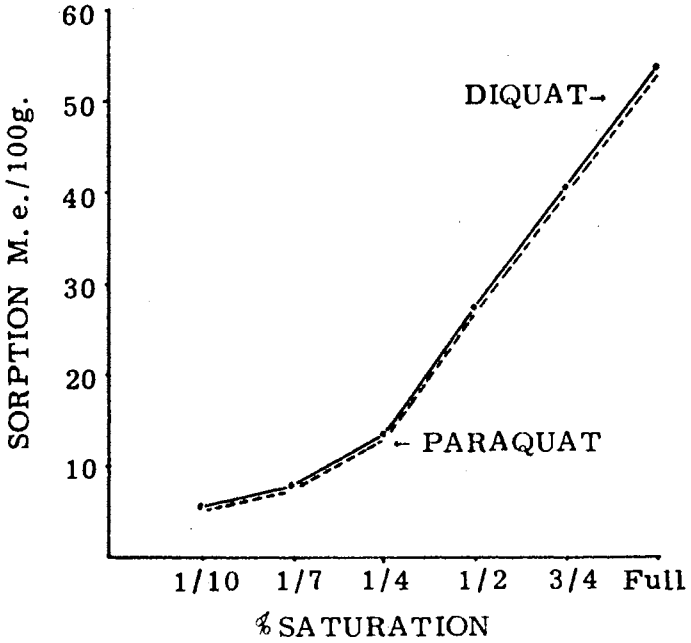


Figure 2. Sorption of Diquat and Paraquat by Beidellite (2-.2μ)

TABLE V

SORPTION OF DIQUAT AND PARAQUAT BY ARIZONA BENTONITE (M.e./100g. OF C.E.C.)

% Saturation	Arizona Bentonite					
	Diquat			Paraquat		
	> 2μ	2-.2μ	<.2μ	> 2μ	2-.2μ	<.2μ
Full	113.26	100.30	102.02	113.17	100.28	100.07
3/4	84.89	75.27	61.82	85.02	75.23	61.89
1/2	56.71	50.22	52.30	56.70	50.05	51.88
1/4	28.35	25.05	26.49	28.34	24.95	26.26
1/7	16.17	14.28	14.35	16.17	14.01	13.13
1/10	11.33	10.02	10.32	11.32	9.91	8.76

TABLE VI

SORPTION OF DIQUAT AND PARAQUAT BY WYOMING BENTONITE (M.e./100g. OF C.E.C.)

% Saturation	Wyoming Bentonite					
	Diquat			Paraquat		
	> 2μ	2-.2μ	<.2μ	> 2μ	2-.2μ	<.2μ
Full	23.46	95.56	90.17	23.22	95.86	91.00
3/4	17.41	61.38	67.44	17.81	61.61	66.78
1/2	8.86	47.41	44.70	8.91	47.91	45.40
1/4	4.42	23.97	22.96	4.38	23.97	22.90
1/7	3.31	13.61	13.04	3.32	13.60	13.03
1/10	2.30	9.55	9.16	2.28	9.49	9.09

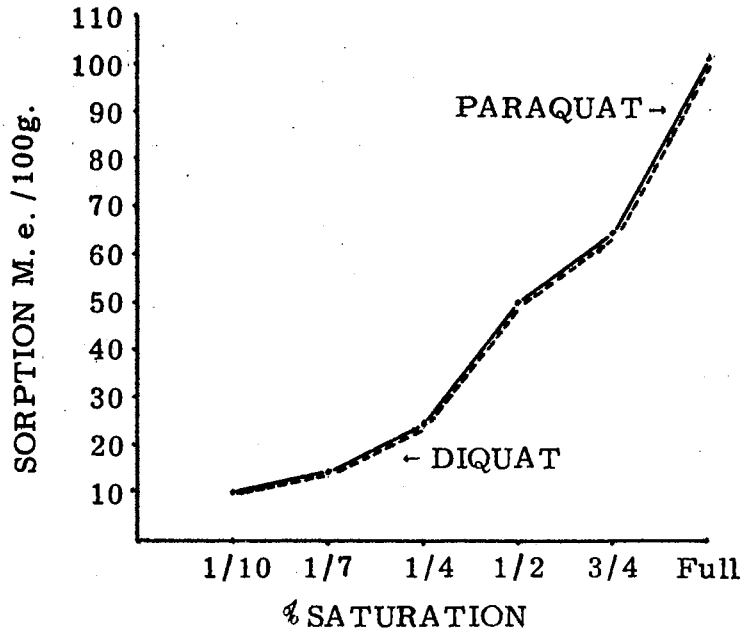


Figure 3. Sorption of Paraquat and Diquat by Arizona Bentonite (2-.2μ)

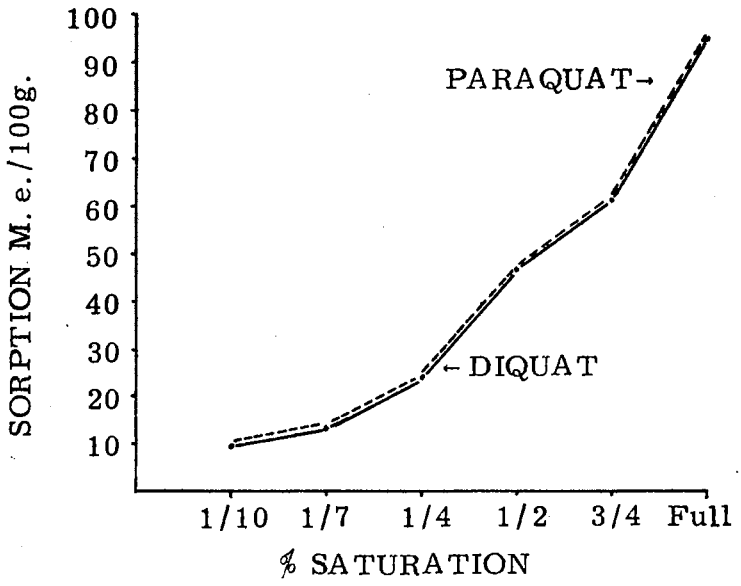


Figure 4. Sorption of Paraquat and Diquat by Wyoming Bentonite (2-.2μ)

TABLE VII

SORPTION OF DIQUAT AND PARAQUAT BY BELLE FOURCHE MONTMORILLONITE (M.e./100g. OF C.E.C.)

% Saturation	Belle Fourche Montmorillonite			
	Diquat		Paraquat	
	> 2μ	< .2μ	> 2μ	< .2μ
Full	76.52	73.95	76.48	73.90
3/4	57.29	55.11	57.22	55.10
1/2	38.16	36.97	38.21	36.81
1/4	19.06	18.35	18.86	18.25
1/7	10.85	10.48	10.68	10.40
1/10	7.54	7.37	7.53	7.31

TABLE VIII

SORPTION OF DIQUAT AND PARAQUAT BY HECTORITE (M. e. /100g. OF C.E.C.)

% Saturation	Hectorite			
	Diquat		Paraquat	
	> 2μ	< .2μ	> 2μ	< .2μ
Full	79.36	114.49	79.26	111.99
3/4	59.30	84.63	59.23	80.66
1/2	39.36	58.96	39.36	57.93
1/4	19.95	29.31	19.96	29.17
1/7	11.35	16.39	11.37	16.15
1/10	7.92	11.66	7.91	11.60

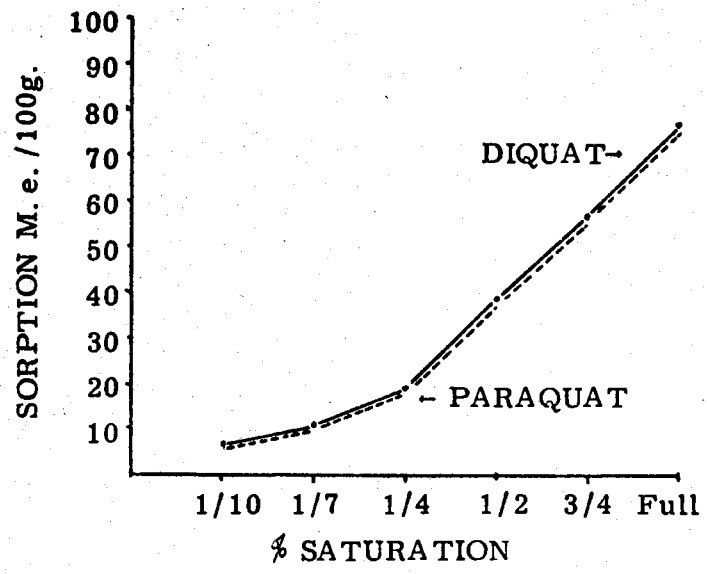


Figure 5. Sorption of Diquat and Paraquat by Belle Fourche Montmorillonite (2-. 2μ)

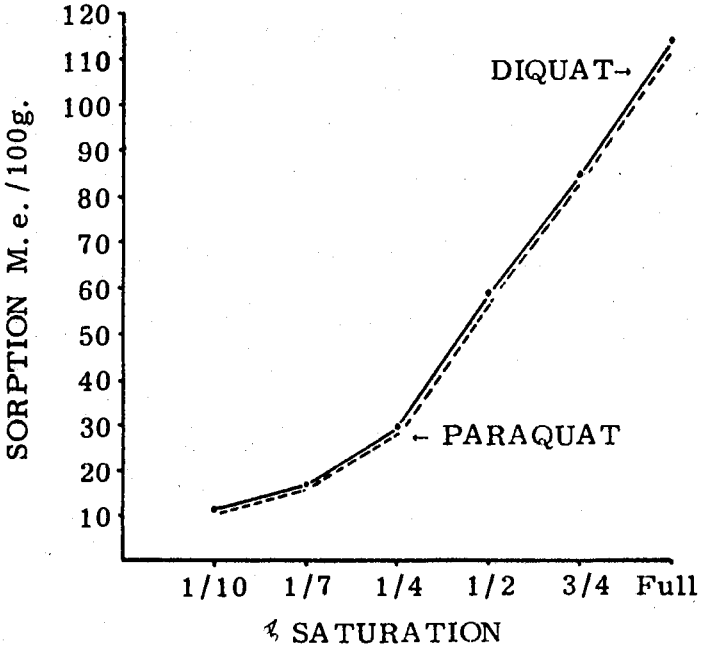


Figure 6. Sorption of Diquat and Paraquat by Hectorite (<. 2μ)

TABLE IX

SORPTION OF DIQUAT AND PARAQUAT BY NONTRONITE (M.e./100g. OF C.E.C.)

% Saturation	Nontronite					
	Diquat			Paraquat		
	> 2μ	2-.2μ	<.2μ	> 2μ	2-.2μ	<.2μ
Full	82.45	83.61	75.48	82.47	82.89	75.31
3/4	61.89	62.63	55.12	61.86	61.86	54.93
1/2	41.26	41.71	36.02	41.24	41.60	35.90
1/4	20.62	20.34	18.84	20.60	20.06	18.76
1/7	11.57	11.85	10.54	11.55	11.82	10.39
1/10	8.24	8.35	7.38	8.11	8.25	7.16

TABLE X

SORPTION OF DIQUAT AND PARAQUAT BY NONTRONITE 35A OR 33A (M. e./100g. OF C. E. C.)

% Saturation	Nontronite 35A or 33A					
	Diquat			Paraquat		
	> 2μ	2-. 2μ	<. 2μ	> 2μ	2-. 2μ	<. 2μ
Full	93.61	89.49	82.87	93.20	89.73	83.80
3/4	70.11	67.22	62.41	69.97	67.41	61.76
1/2	47.00	44.75	42.03	46.95	44.88	41.98
1/4	23.42	22.32	20.88	23.33	22.32	20.74
1/7	11.92	12.65	11.89	11.90	12.66	11.90
1/10	9.38	8.91	8.22	9.35	8.74	8.37

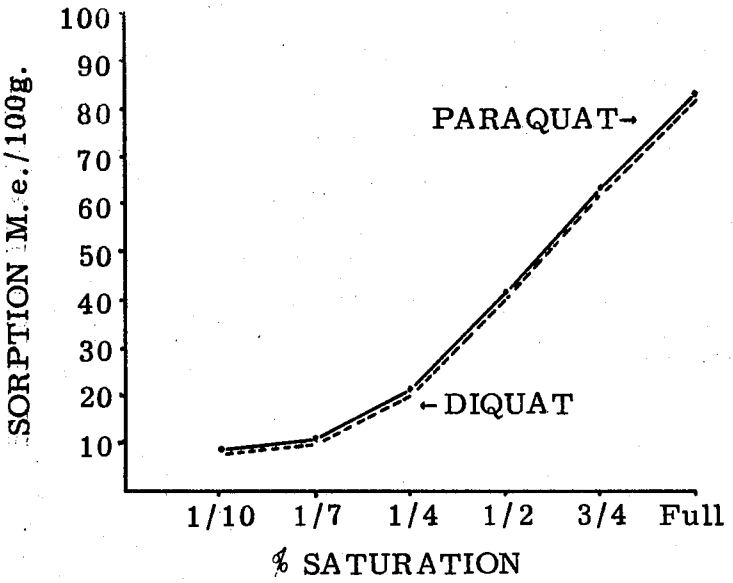


Figure 7. Sorption of Paraquat and Diquat by Nontronite (2-.2μ)

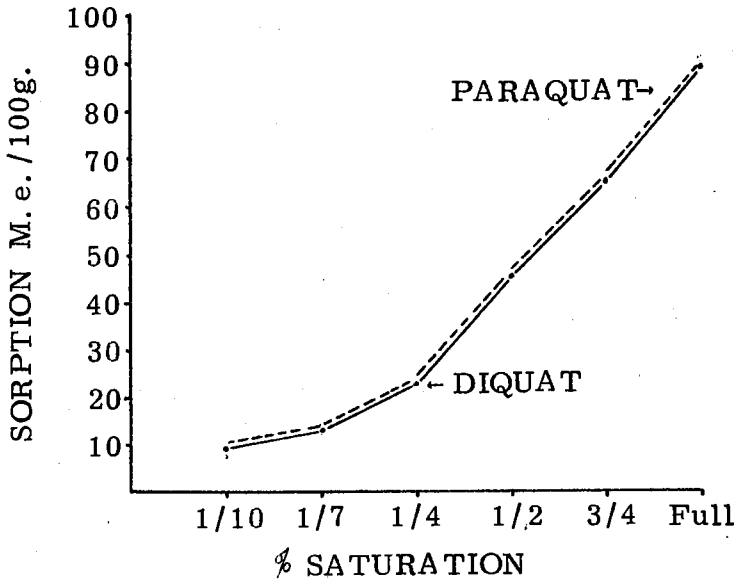


Figure 8. Sorption of Paraquat and Diquat by Nontronite 35A or 33A (2-.2μ)

TABLE XI

SORPTION OF DIQUAT AND PARAQUAT BY VERMICULITE (M. e./100g. OF C. E. C.)

% Saturation	Vermiculite					
	Diquat			Paraquat		
	> 2μ	2-. 2μ	< . 2μ	> 2μ	2-. 2μ	< . 2μ
Full	101.67	112.96	95.23	101.63	112.67	91.91
3/4	76.22	84.51	71.75	76.17	87.22	68.07
1/2	50.79	56.24	44.38	50.72	55.82	43.25
1/4	25.33	27.50	24.54	25.39	28.00	24,52
1/7	14.45	15.95	14.32	14.52	15.82	13.83
1/10	10.16	11.20	10.01	10.16	11.10	9.63

TABLE XII

SORPTION OF DIQUAT AND PARAQUAT BY FITHIAN ILLITE (M. e./100g. OF C. E. C.)

% Saturation	Fithian Illite					
	Diquat			Paraquat		
	> 2μ	2-. 2μ	< . 2μ	> 2μ	2-. 2μ	< . 2μ
Full	8.75	9.73	83.74	8.64	9.58	79.33
3/4	6.43	7.19	59.89	6.36	7.20	55.05
1/2	4.28	4.91	40.53	4.28	4.86	36.59
1/4	2.14	2.42	21.49	2.16	2.41	16.51
1/7	1.24	1.36	12.47	1.22	1.35	12.13
1/10	.85	.89	7.07	.84	.87	6.41

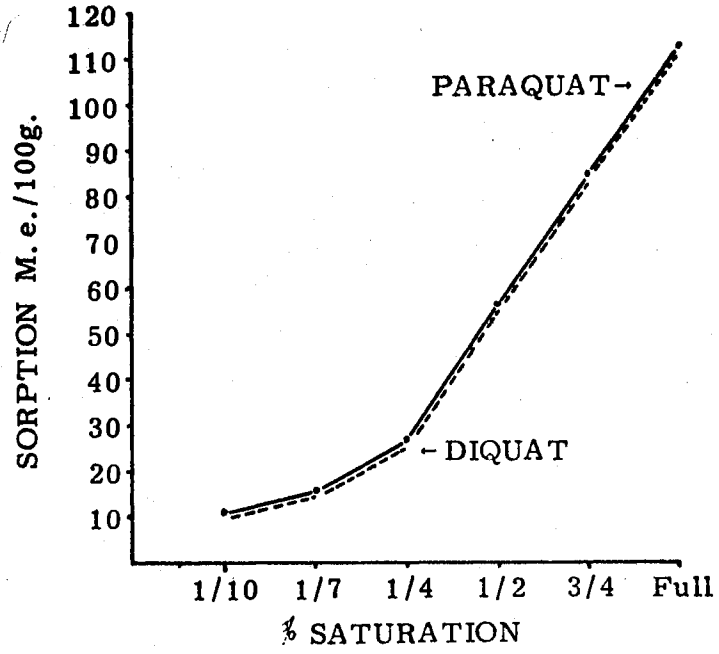


Figure 9. Sorption of Paraquat and Diquat by Vermiculite (2-.2μ)

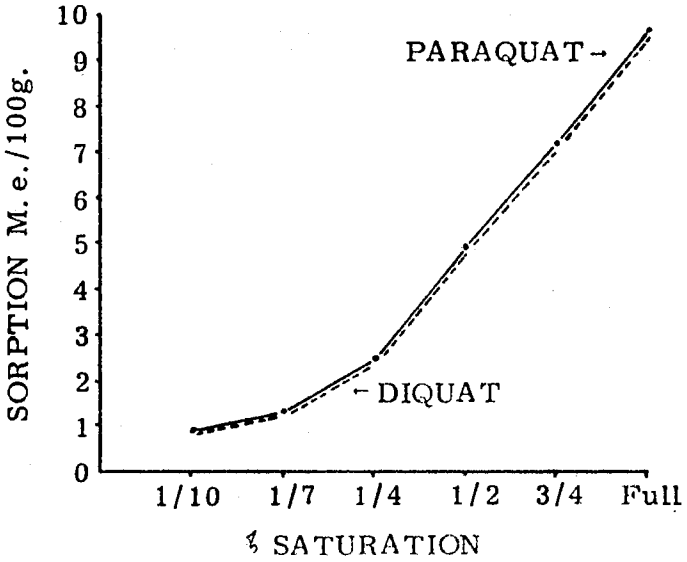


Figure 10. Sorption of Paraquat and Diquat by Fithian Illite (2-.2μ)

illite (Table XII). The paraquat and diquat were probably sorbed around the edges of Fithian illite just like attapulgite due to broken bonds or substitution within the structure. Diquat sorption exceeds paraquat sorption, probably due to the smaller size of the diquat ions (Figure 10).

The coarse fractions of Fithian illite sorbed more diquat and paraquat than fine fractions of illite.

5. Sorption of diquat and paraquat by Georgia kaolinite. Georgia kaolinite is a nonexpanding type of clay mineral. The organic cations were sorbed on the edges or faces of the clay particles rather than in the interiors of the structure. This sorption is probably due mainly to the broken bond charges of the clay. Georgia kaolinite sorbed paraquat and diquat in amounts close to the C. E. C. of the clay (Table XIII). The coarse clay sorbed more paraquat and diquat than did the fine clay. Diquat sorption exceeds paraquat sorption, probably due to the smaller size of the diquat ions (Figure 11).

6. Sorption of diquat and paraquat by Stillwater volcanic ash. Bailey and White (2) reported that the clay minerals illite, kaolinite and chlorite, because of their low cation exchange capacity and surface area, would not have as large a sorption capacity as montmorillonite and vermiculite. However, this was not the case with Stillwater volcanic ash which had a low cation exchange capacity. The sorption of Stillwater volcanic ash was greater than that for most of the montmorillonites and vermiculites which were investigated in this study. The Stillwater volcanic ash sorbed paraquat and diquat in amounts very close to the C. E. C. of the clay (Table XIV). The organic cations were probably sorbed on the edges of the clay particles, due mainly to

TABLE XIII

SORPTION OF DIQUAT AND PARAQUAT BY GEORGIA KAOLONITE (M. e./100g. OF C.E.C.)

% Saturation	Georgia Kaolonite					
	Diquat			Paraquat		
	> 2μ	2-.2μ	<.2μ	> 2μ	2-.2μ	<.2μ
Full	5.80	13.20	59.80	5.76	13.50	58.62
3/4	4.32	9.68	44.08	4.25	9.95	42.07
1/2	2.85	5.78	28.10	2.81	6.14	31.54
1/4	1.41	2.61	14.98	1.39	3.03	15.68
1/7	.73	1.84	8.82	.81	1.80	8.64
1/10	.55	1.25	6.01	.57	1.14	.59

TABLE XIV

SORPTION OF DIQUAT AND PARAQUAT BY VOLCANIC ASH (STILLWATER) (M. e./100g. OF C. E. C.)

% Saturation	Stillwater Volcanic Ash					
	Diquat			Paraquat		
	> 2μ	2-.2μ	<.2μ	>2μ	2-.2μ	<.2μ
Full	4.84	26.68	56.13	4.83	26.50	55.40
3/4	3.62	20.64	41.52	3.61	20.64	41.66
1/2	2.42	13.40	28.59	2.42	13.37	28.56
1/4	1.21	6.69	15.42	1.20	6.68	15.27
1/7	.71	3.90	8.79	.71	3.38	8.66
1/10	.49	2.78	5.70	.49	2.70	5.66

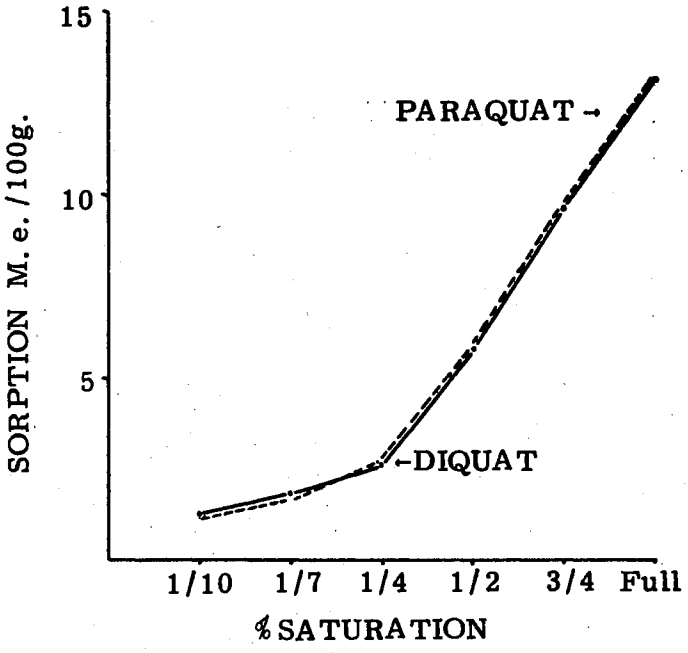


Figure 11. Sorption of Paraquat and Diquat by Georgia Kaolinite (2-. 2μ)

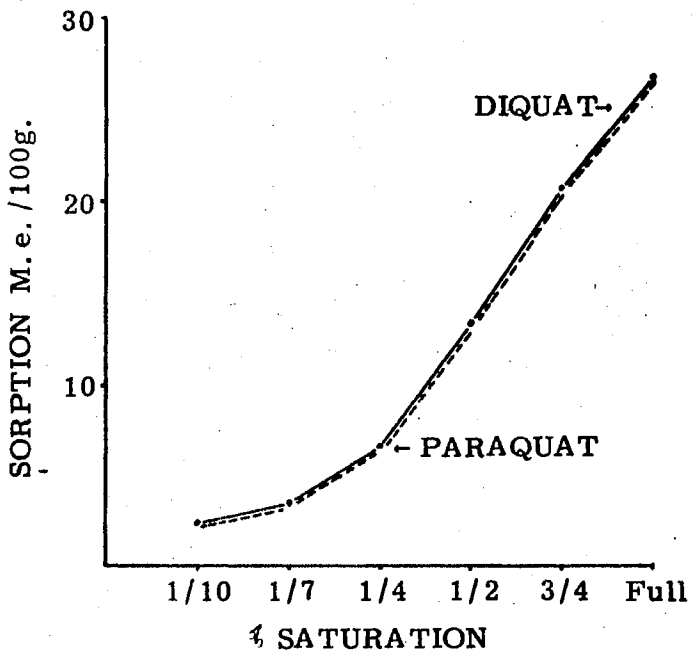


Figure 12. Sorption of Diquat and Paraquat by Volcanic Ash (Stillwater)(2-.2μ)

broken bonds and substitution within the clay structure. Diquat sorption exceeds paraquat sorption, probably due to the smaller size of the diquat ions (Figure 12).

The cation exchange capacity of all the mineral clays investigated in this study was very close to the C. E. C. obtained by saturation with diquat and paraquat. This indicates that sorption of paraquat and diquat could possibly be used for an accurate determination of the cation exchange capacity (C. E. C.) of soil clay minerals.

X-ray Diffraction Analysis

X-ray diffraction patterns of clay minerals studied are shown in Figures 13 through 35 and the following observations were made.

X-ray Diffraction Pattern of Attapulgite

Saturation of clay samples with diquat and paraquat had little if any effect on attapulgite. The d-spacing of Mg saturated attapulgite was the same as the d-spacing obtained by saturating with different amounts of diquat and paraquat (Figures 13 and 14). This probably was due to the structure of attapulgite which consists of double silica chains running parallel to the C axis with the chains linked together through oxygens at their longitudinal edges (4). Therefore, paraquat and diquat were sorbed around the edges of the attapulgite particle and did not increase or decrease the 2θ value or the d-spacing value of attapulgite. The sorption was probably due to broken bond charges of attapulgite. Attempts were made to remove the Al-interlayer of attapulgite, saturate with paraquat and study the x-ray diffraction pattern. It was

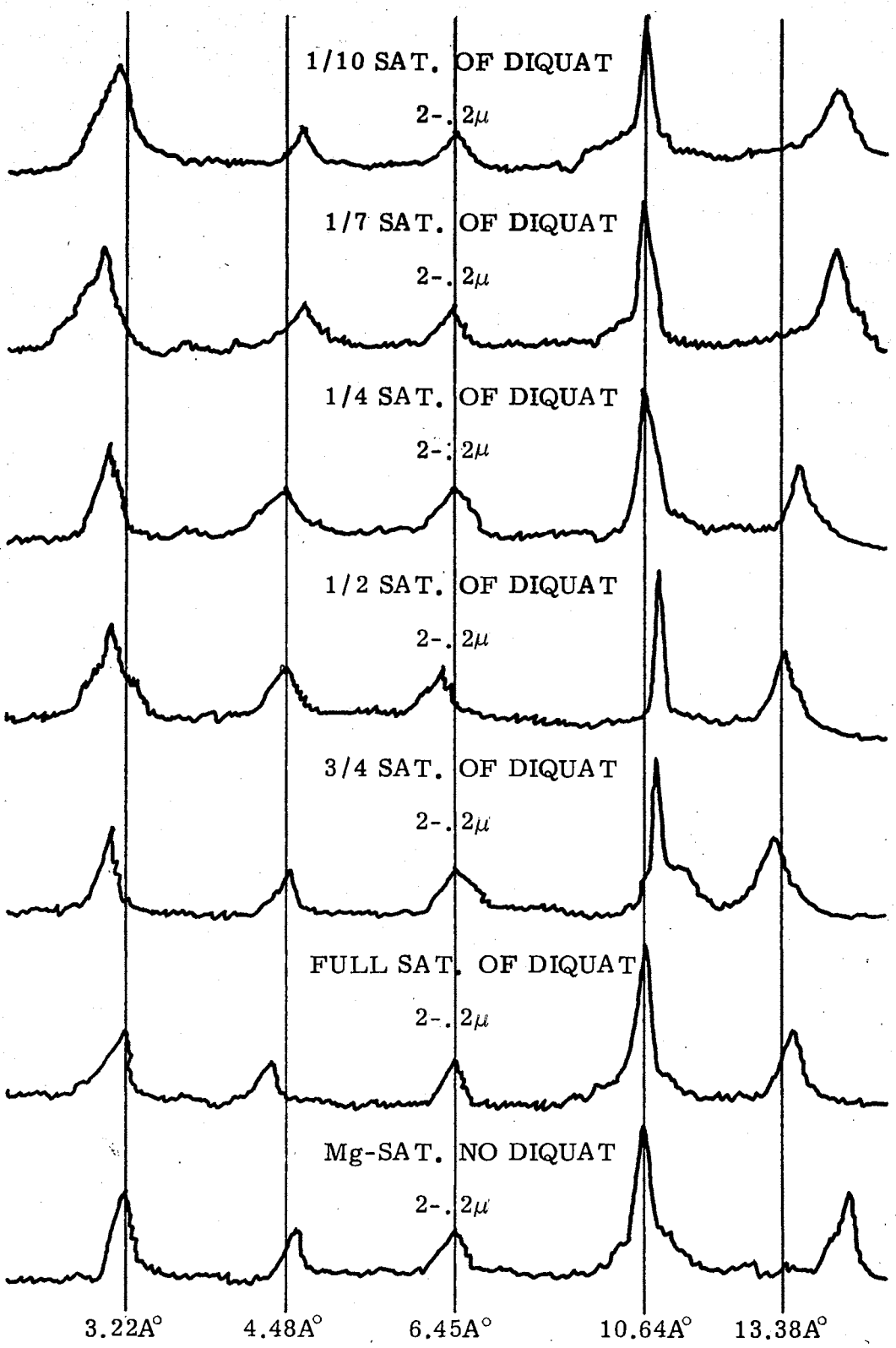


Figure 13. X-ray Diffraction Pattern of Coarse Clay (2-.2μ) of Attapulgite Saturated with Different Fractions of Diquat

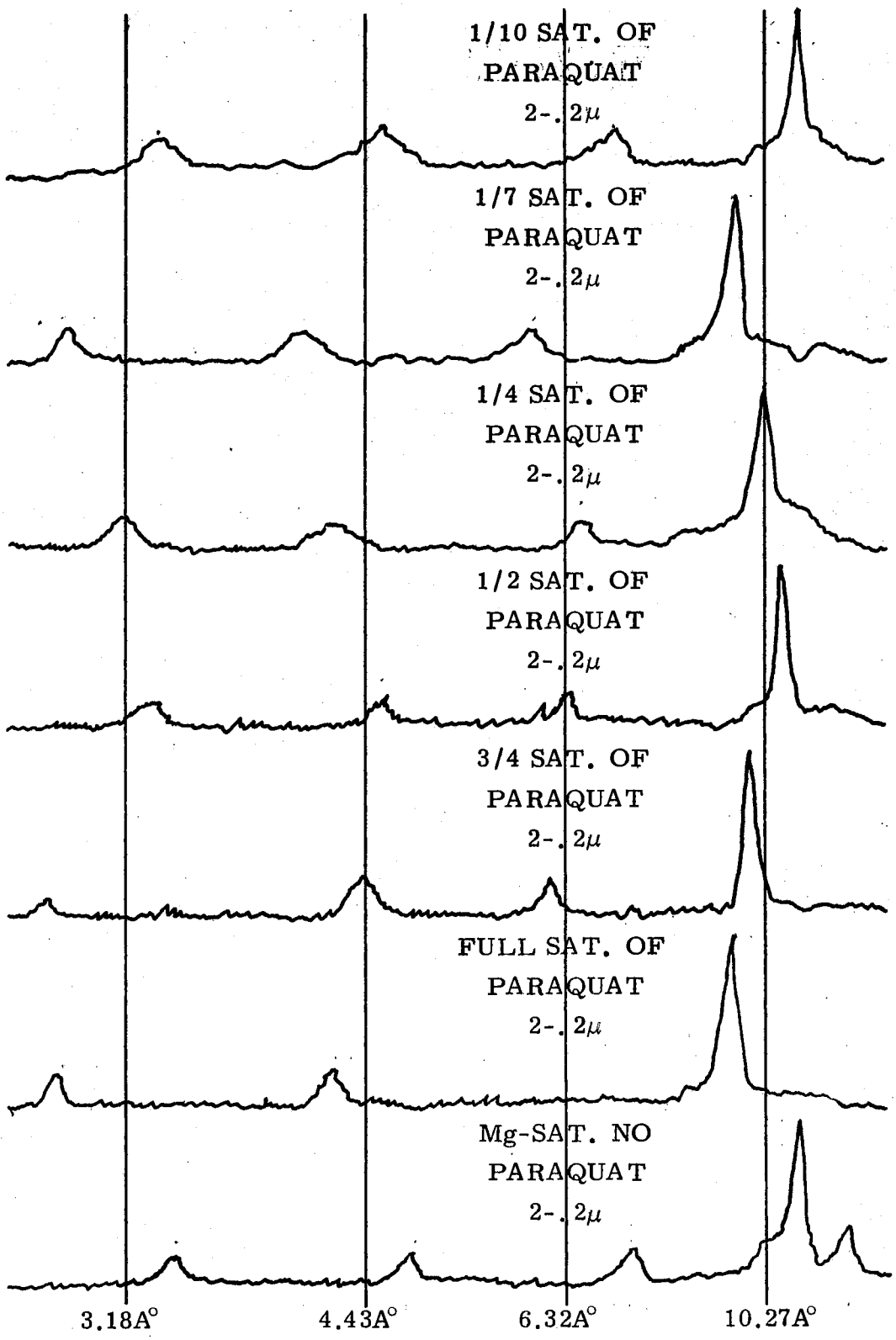


Figure 14. X-ray Diffraction Pattern of Coarse Clay (2-.2μ) of Attapulgite Saturated with Different Fractions of Paraquat

found that no Aℓ-interlayer was present in the attapulgite and x-ray results were the same as indicated above.

X-ray Diffraction Pattern of the Montmorillonite Group

Giesking (6) showed that the (00ℓ) interplanar spacing of clay minerals saturated with organic cations depends upon the organic cation present in the clay, but in a manner that apparently is not determined by the structure of the ion. Presumably the organic molecules are situated, at least in part, between the alumino silicate layers. A later study by Weber et al. (21) shows by x-ray analysis that diquat and paraquat are held in the structure of montmorillonite with the plane of the ring parallel to the silicate sheet. The results of this study show that paraquat and diquat are held in the structure of montmorillonite, which indicates that practically all of the free water in the structure was displaced by the paraquat and diquat and which was probably responsible for a decrease in the d-spacing of the montmorillonite clays. Later attempts were made to remove the Aℓ-interlayers of montmorillonite clays and then fully saturate with paraquat. The results were not changed because no Aℓ-interlayers were present in the montmorillonite clays. The x-ray diffraction pattern results were the same as obtained previously.

1. Beidellite. Beidellite is an isomorphous series of the montmorillonite group. The main difference is that in montmorillonite the primary structure replacement is that of Mg^{+2} for $A\ell^{+3}$; in beidellite the substitution of $A\ell^{+3}$ for Si^{+4} predominates.

The x-ray diffraction patterns of beidellite are shown in Figures 15 and 16. Full, 3/4 and 1/2 saturation of paraquat and diquat

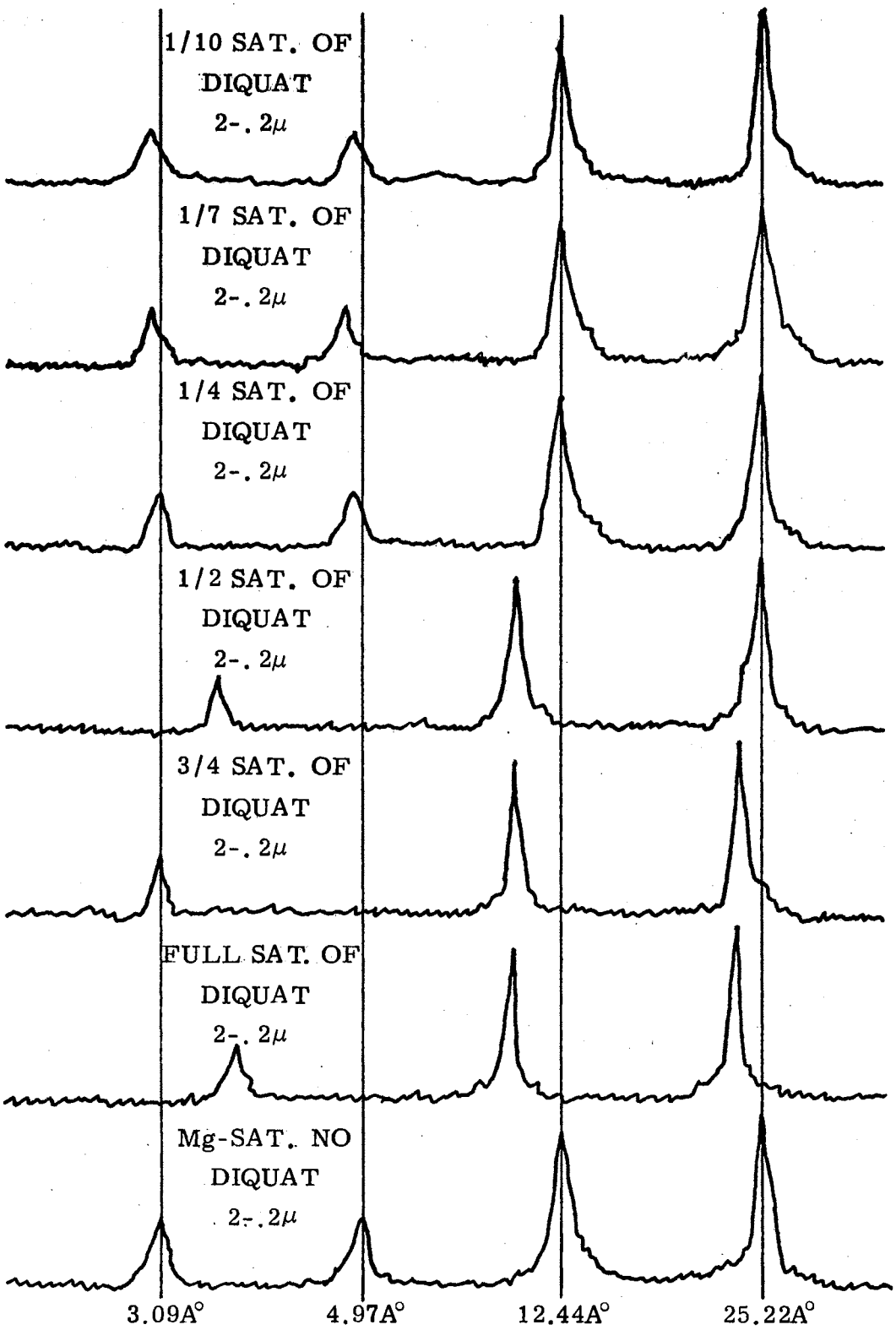


Figure 15. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Indian Beidellite Saturated with Different Fractions of Diquat

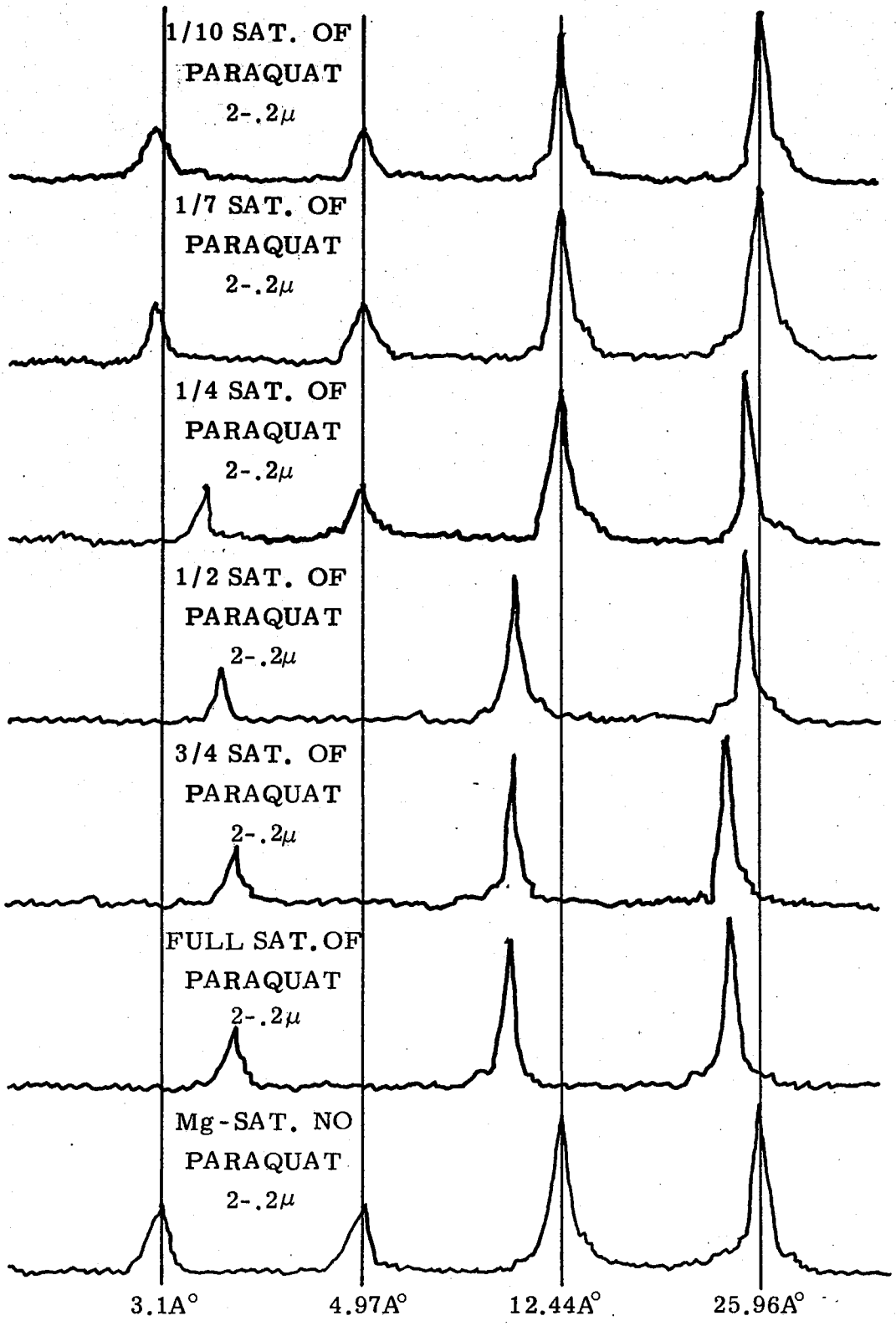


Figure 16. X-ray Diffraction Pattern of Coarse Clay (2-.2μ) of Indian Beidellite Saturated with Different Fractions of Paraquat

decreases the d-spacing of beidellite from 25.96A° to 23.23A° and from 12.44A° to 11.41A°. The saturation rates of 1/10, 1/7 and 1/4 for paraquat and diquat did not have any effect on the d-spacing of beidellite. Chlorite (second order maximum), 4.97A° peak collapsed when clay was saturated with 1/2, 3/4 and full saturation of paraquat and diquat. Clay minerals saturated with diquat and paraquat had the same d-spacing pattern.

2. Arizona bentonite. The x-ray diffraction patterns of Arizona bentonite are shown in Figures 17 and 18. Full and 3/4 saturation of paraquat decreases the d-spacing of Arizona bentonite from 15.76A° to 12.8A°, but the diffraction peak increases in intensity. As the percentage of saturation of paraquat decreased, the d-spacing of Arizona bentonite increases and 1/7 and 1/10 saturation of paraquat had little or no effect on d-spacing of the clay mineral. The saturation rates of 1/7 and 1/10 for diquat had little effect on d-spacing and decreased the diffraction peak from 15.76A° to 15.22A°. This indicates that a small amount of diquat may have been displaced within the clay structure. Full and 3/4 saturation of the clay by diquat caused the diffraction peak to decrease from 15.76A° to 13.38A°. Paraquat was preferentially sorbed over diquat.

3. Wyoming bentonite. The x-ray diffraction patterns of Wyoming bentonite are shown in Figures 19 and 20. Full saturation of this clay with paraquat decreases the d-spacing of Wyoming bentonite from 15.49A° to 12.98A°. Saturation rates of 1/7 and 1/10 for paraquat did not have any effect on d-spacing and even saturations of 1/4, 1/2 and 3/4 had very little effect on d-spacing. Chlorite (second order diffraction maximum), 5.09A° peak collapsed as clays were saturated

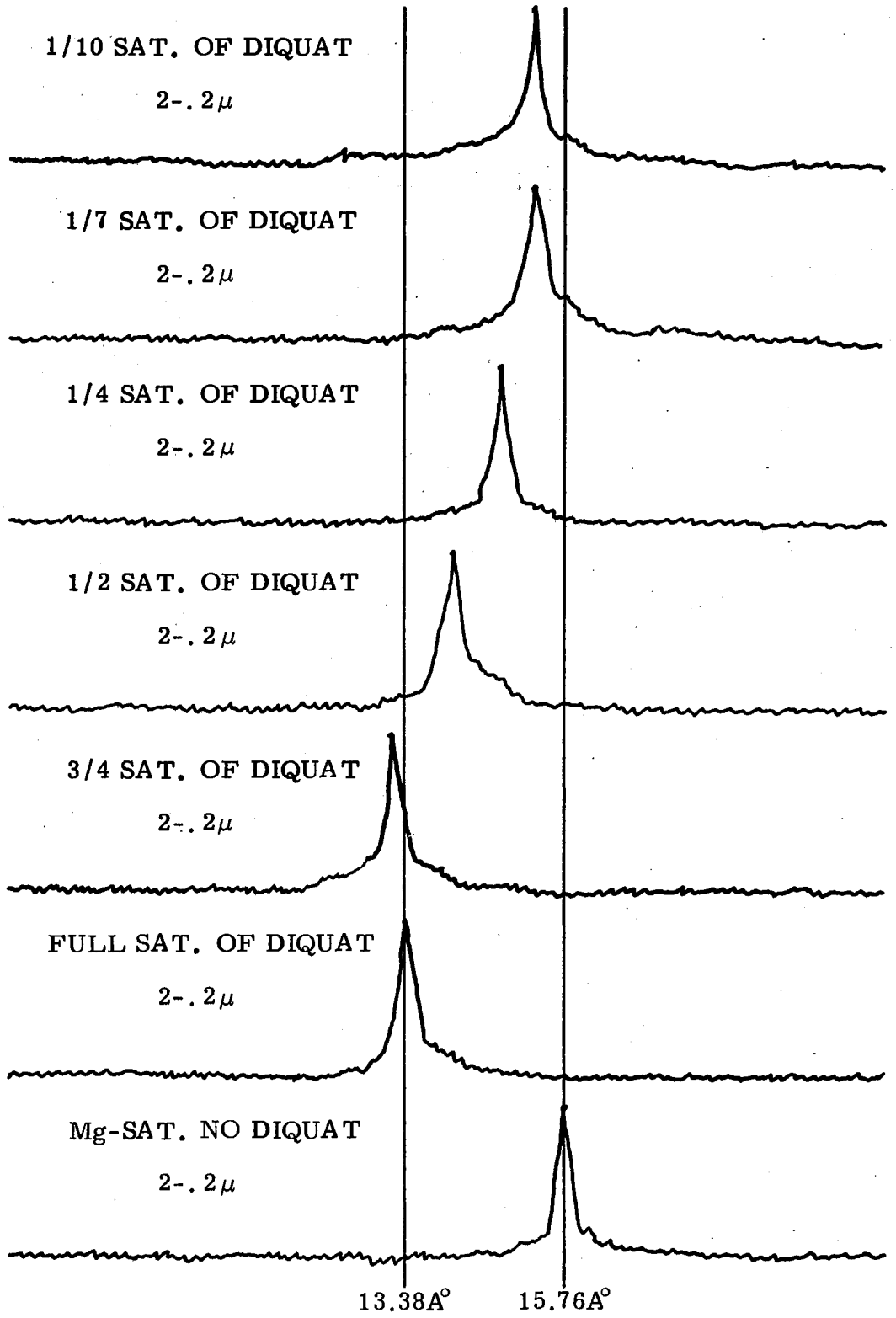


Figure 17. X-ray Diffraction Pattern of Coarse Clay (2-.2μ) of Arizona Bentonite Saturated with Different Fractions of Diquat

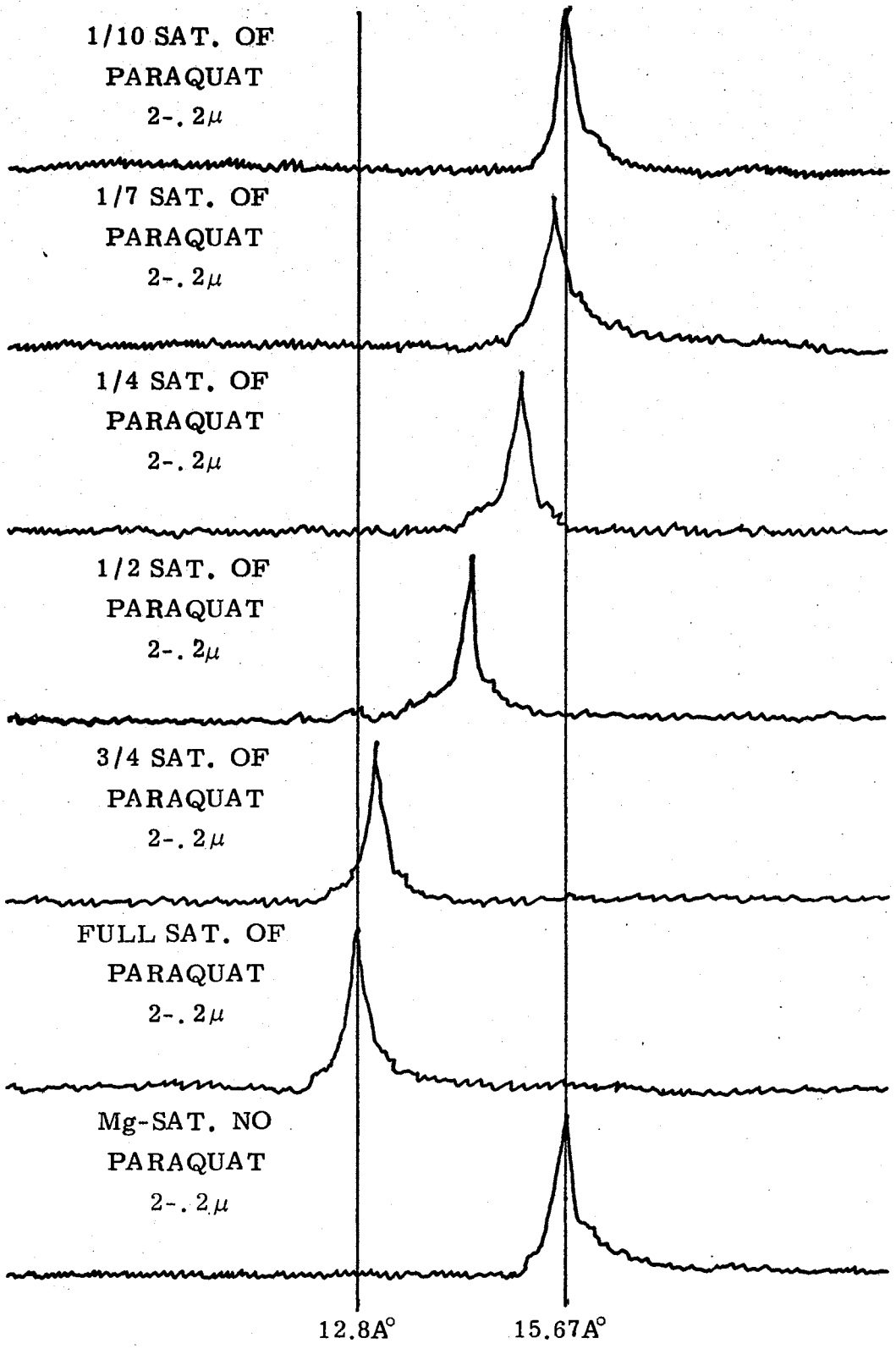


Figure 18. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Arizona Bentonite Saturated with Different Fractions of Paraquat

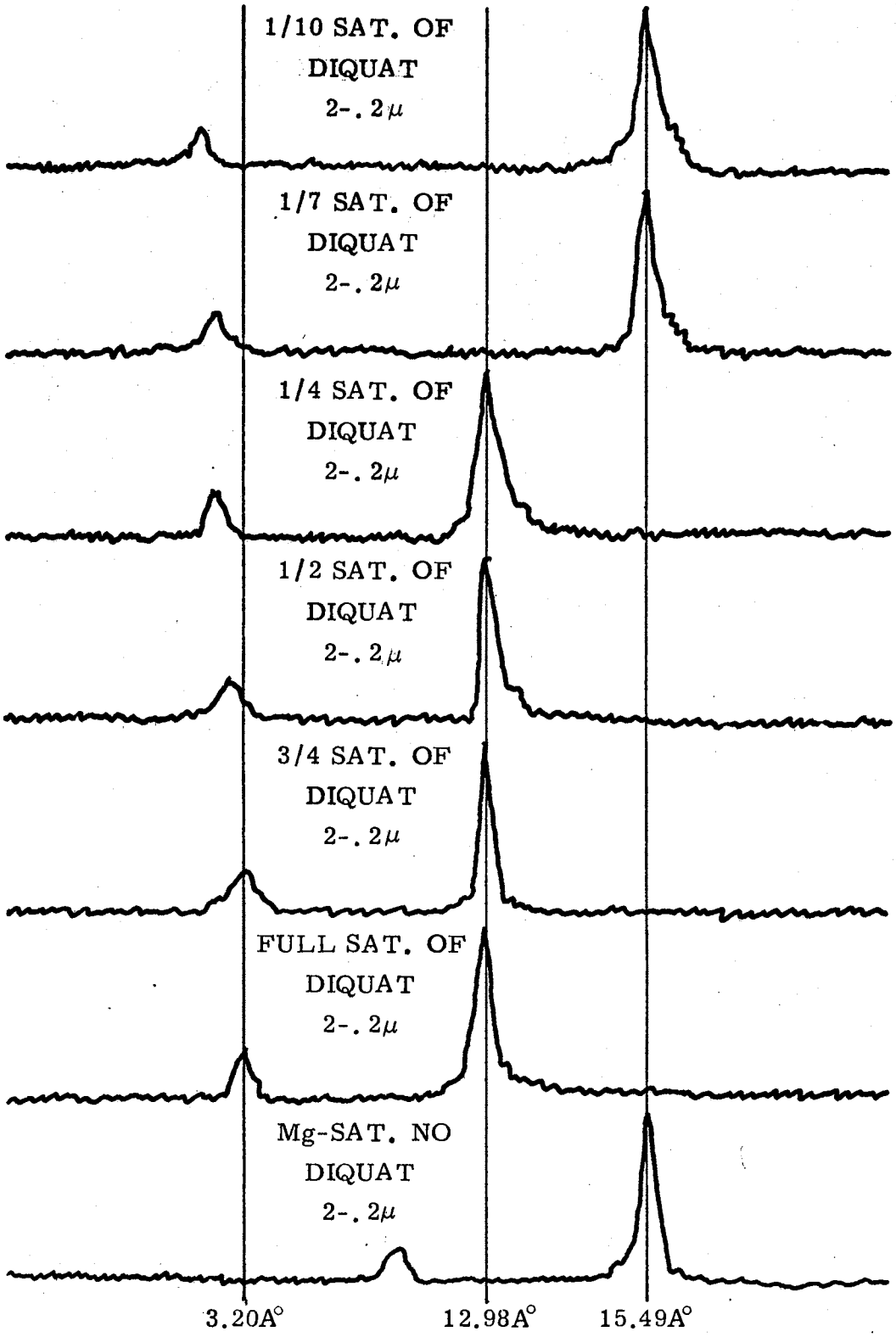


Figure 19. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Wyoming Bentonite Saturated with Different Fractions of Diquat

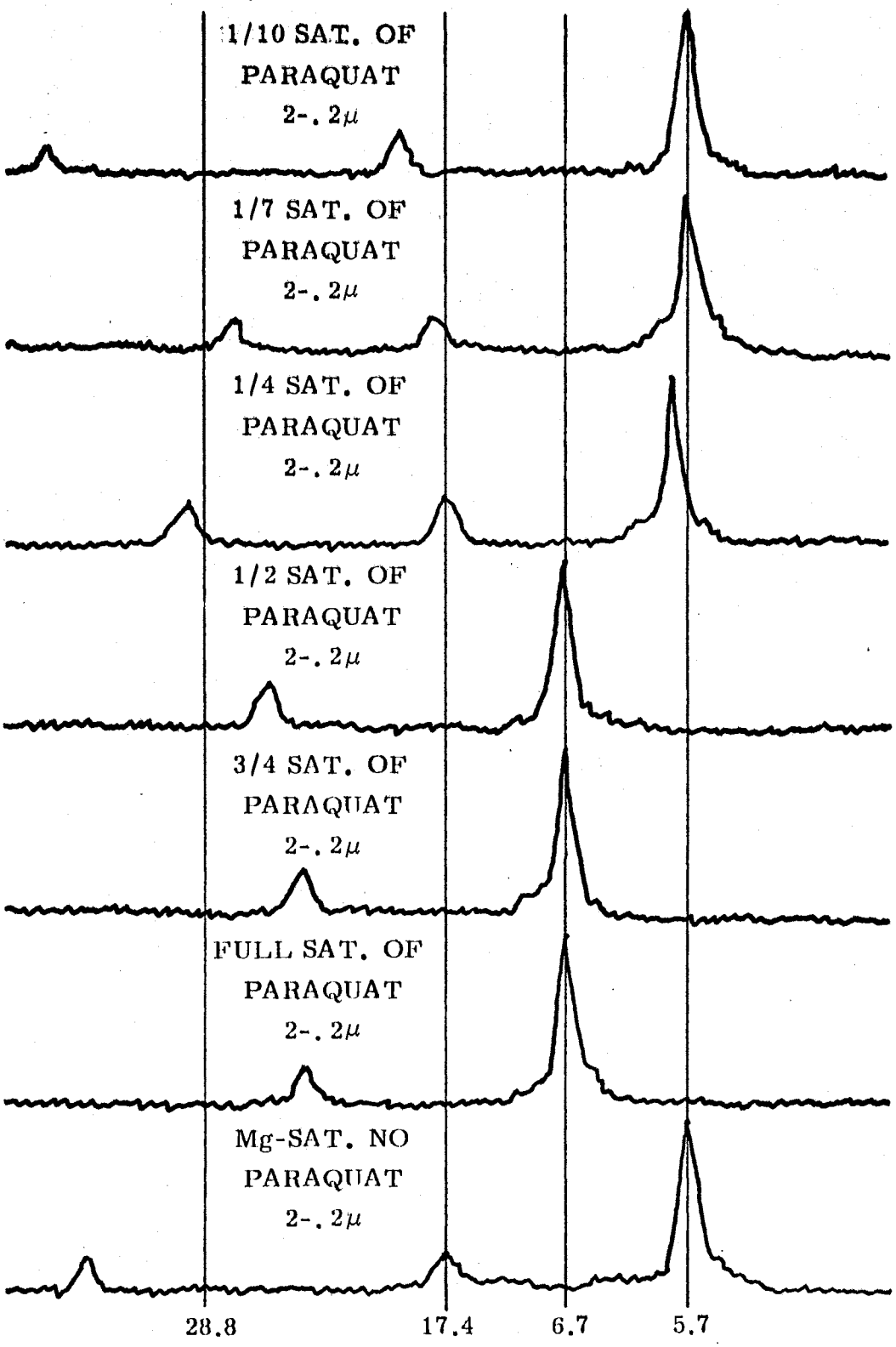


Figure 20. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Wyoming Bentonite Saturated with Different Fractions of Paraquat

with 1/4, 1/2, 3/4 and full fractions of paraquat. Diquat saturation had the same effect on the clay mineral as paraquat, except that 5.09A° chlorite (second order maximum) did not appear in any of the fractions of the diquat saturated clay.

4. Belle Fourche montmorillonite. The x-ray diffraction patterns of Belle Fourche montmorillonite are shown in Figures 21 and 22. Full saturation of diquat and paraquat decreases the d-spacing of Belle Fourche montmorillonite from 15.49A° to 12.98A°. Saturation of 1/10, 1/7 and 1/4 for diquat and paraquat did not have any effect on the d-spacing of the clay, and 3/4 and 1/2 saturation had little effect. This indicated that diquat and paraquat were 100% sorbed by the clay and there was no additional ion exchange between the organic cation and the clay. Chlorite (second order maximum), 5.09A° peak collapsed as the clay was saturated with 1/2, 3/4 and full fractions of diquat and paraquat.

5. Hectorite. The x-ray diffraction patterns of hectorite are shown in Figures 23 and 24. Full, 3/4, 1/2 and 1/4 saturations of diquat and paraquat decreases the d-spacing of hectorite from 15.22A° to 13.18A°. Saturation rates of 1/7 and 1/10 for paraquat had little effect on d-spacing of hectorite; however, the diffraction maximum decreased from 15.22A° to 14.71A°. Diquat and paraquat saturation samples had the same d-spacing patterns.

6. Nontronite. Nontronite is a member of the isomorphic series of the montmorillonite group. In most of the minerals of the nontronite series, the substitution is iron for aluminum.

The x-ray diffraction patterns of nontronite are shown in Figures 25 and 26. Full and 3/4 saturation of paraquat decreases the d-spacing

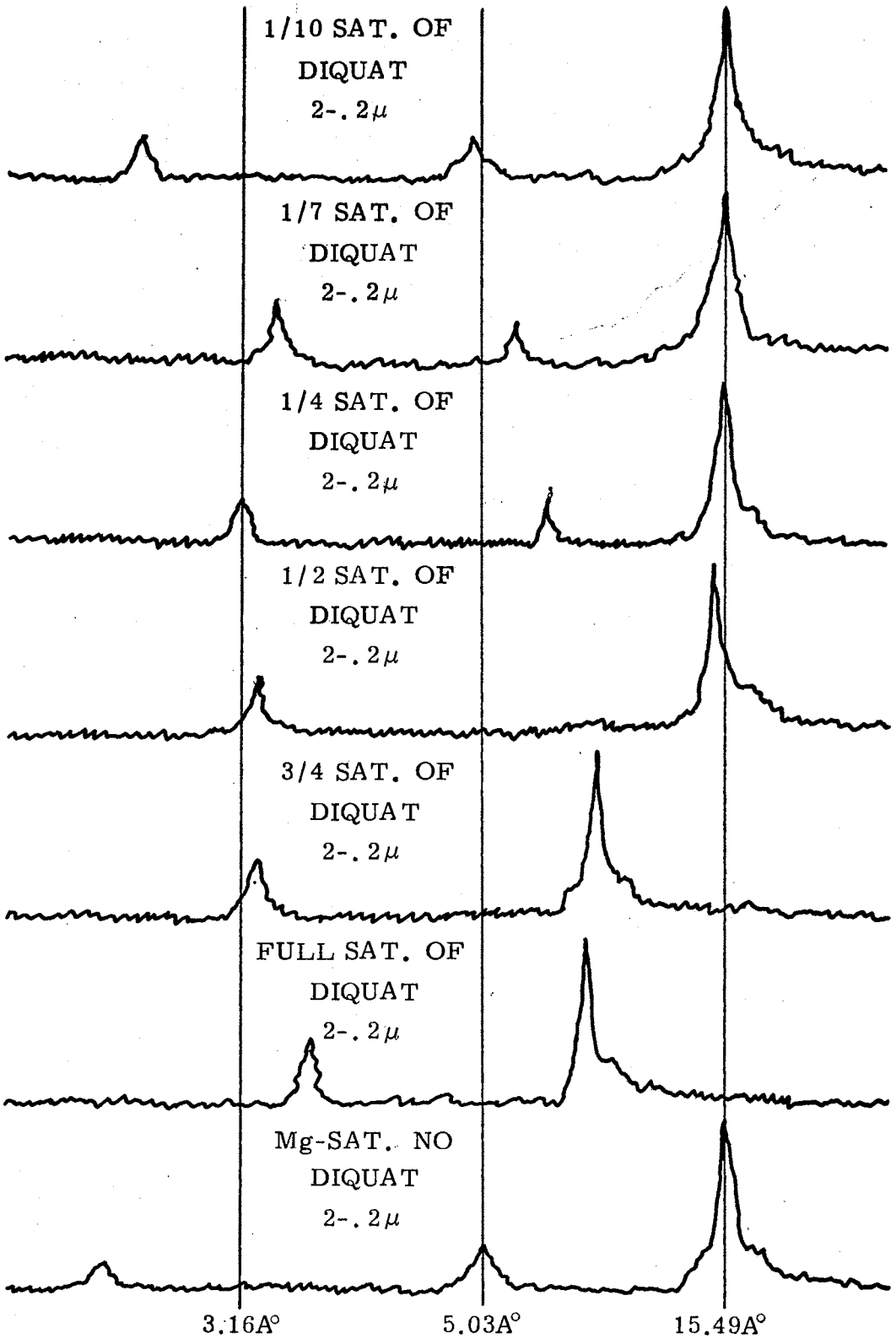


Figure 21. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Belle Fourche Montmorillonite Saturated with Different Fractions of Diquat

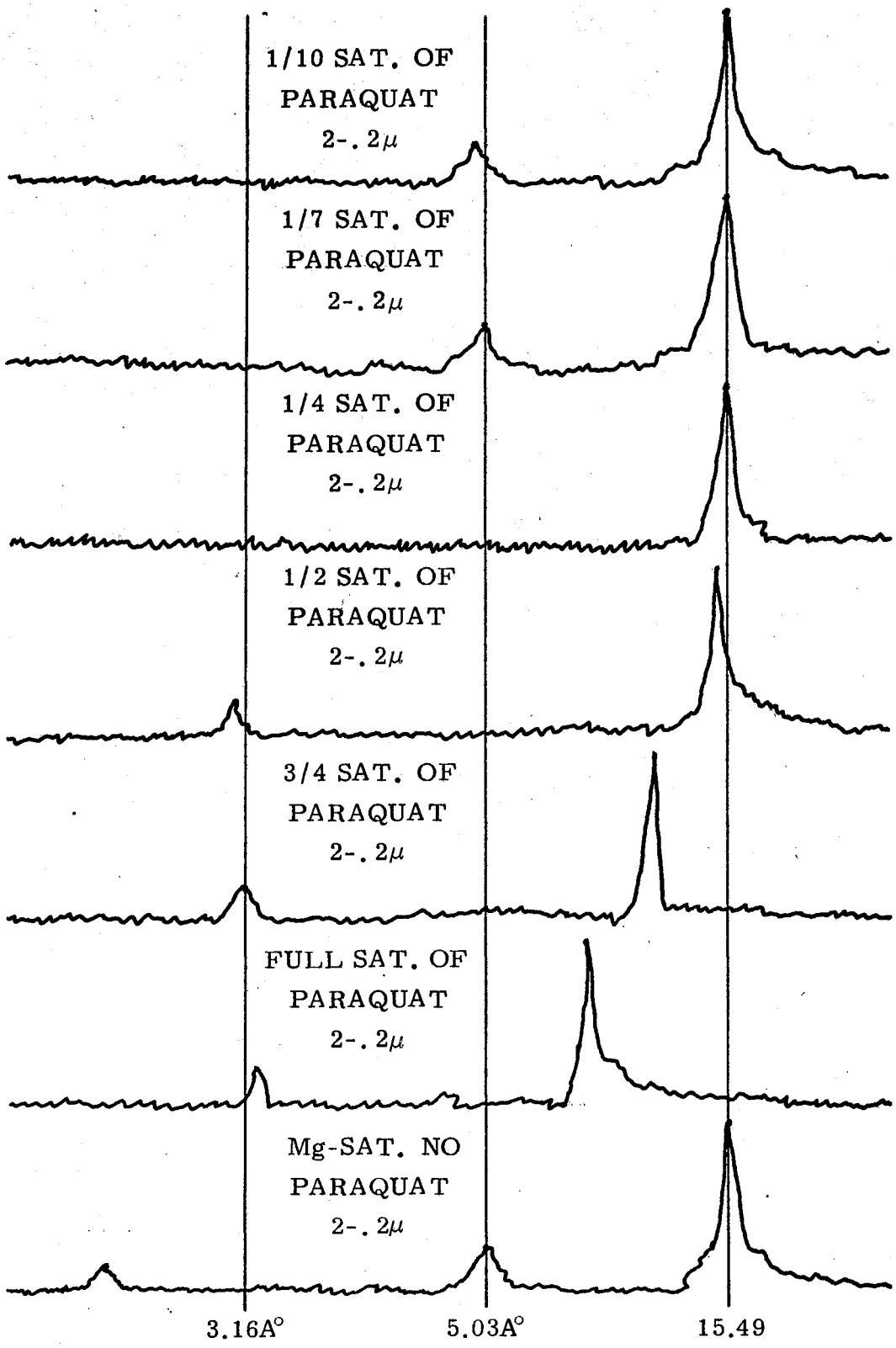


Figure 22. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Belle Fourche Montmorillonite Saturated with Different Fractions of Paraquat

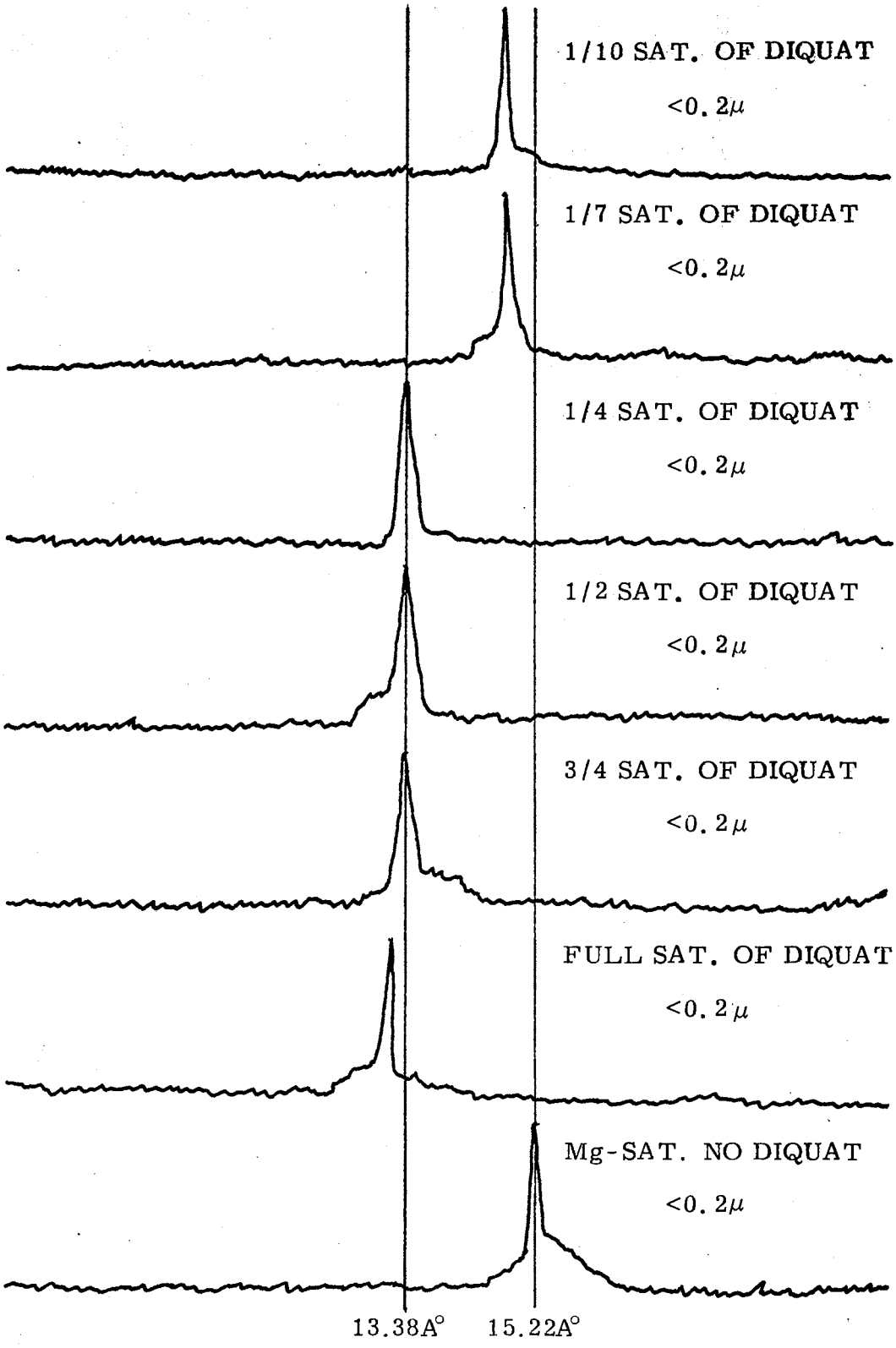


Figure 23. X-ray Diffraction Pattern of Fine Clay (<0.2μ) of Hectorite Saturated with Different Fractions of Diquat

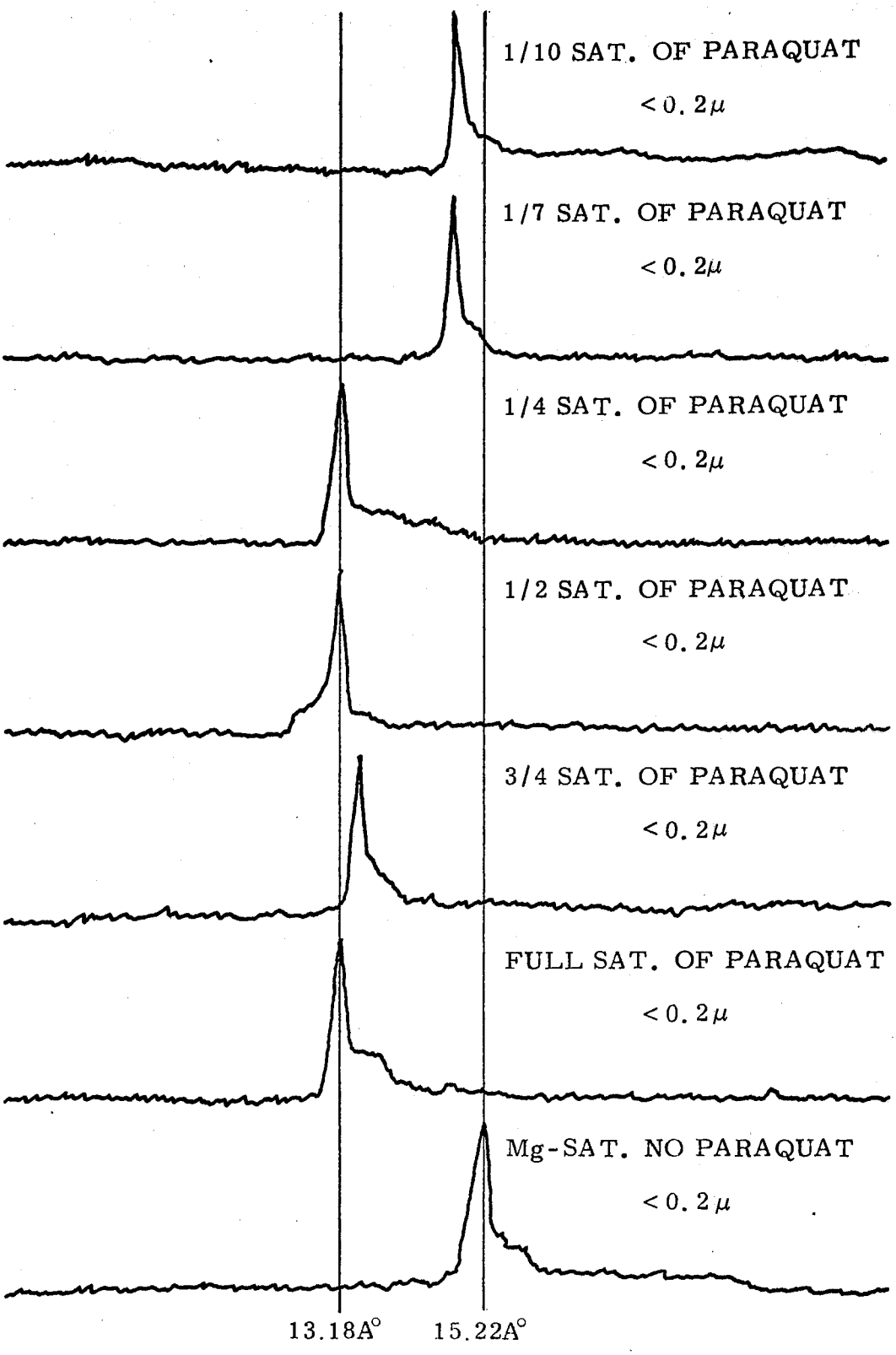


Figure 24. X-ray Diffraction Pattern of Fine Clay (< 0.2μ) of Hectorite Saturated with Different Fractions of Paraquat

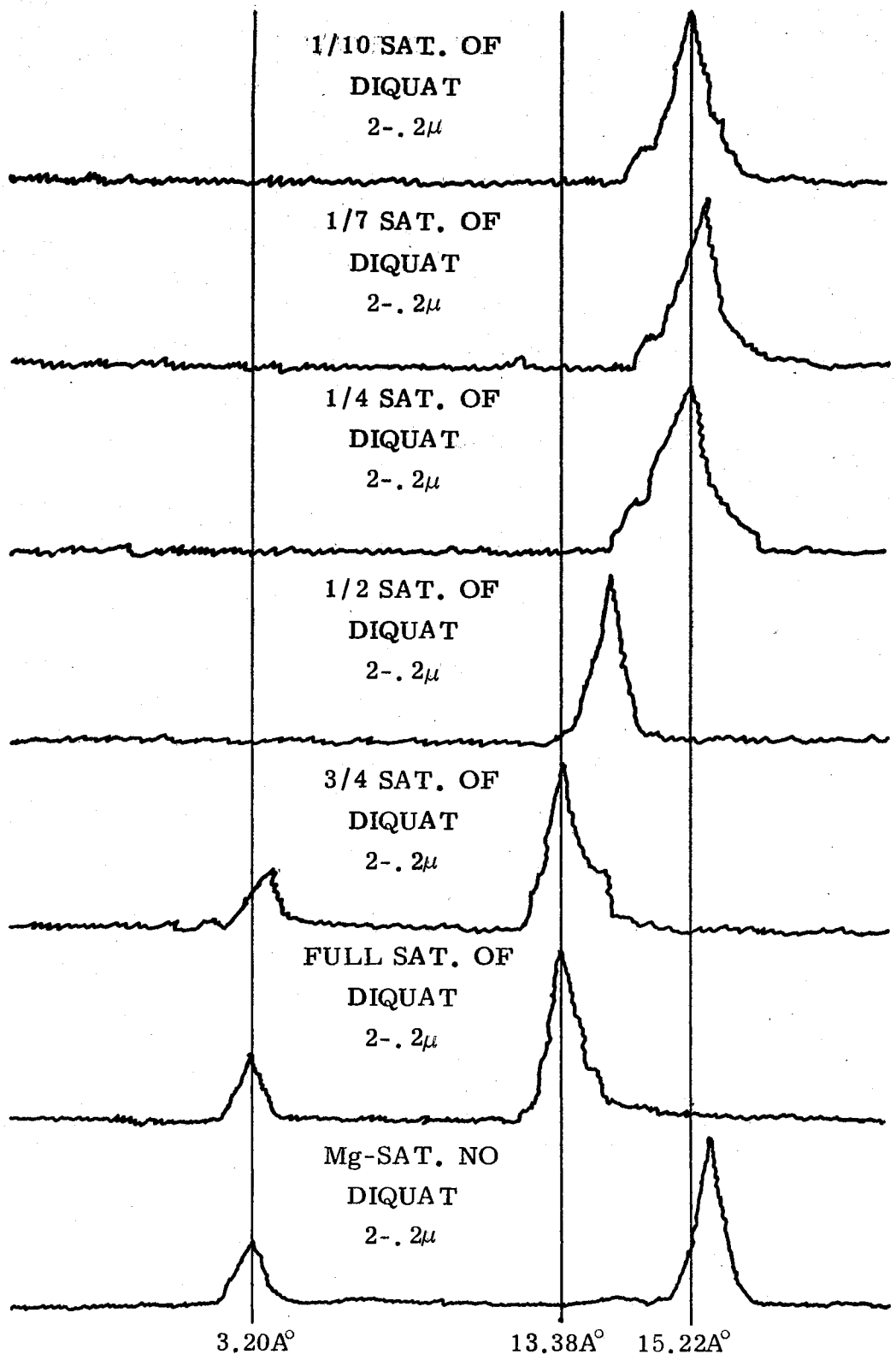


Figure 25. X-ray Diffraction Pattern of Coarse Clay (2-.2μ) of Nontronite Saturated with Different Fractions of Diquat

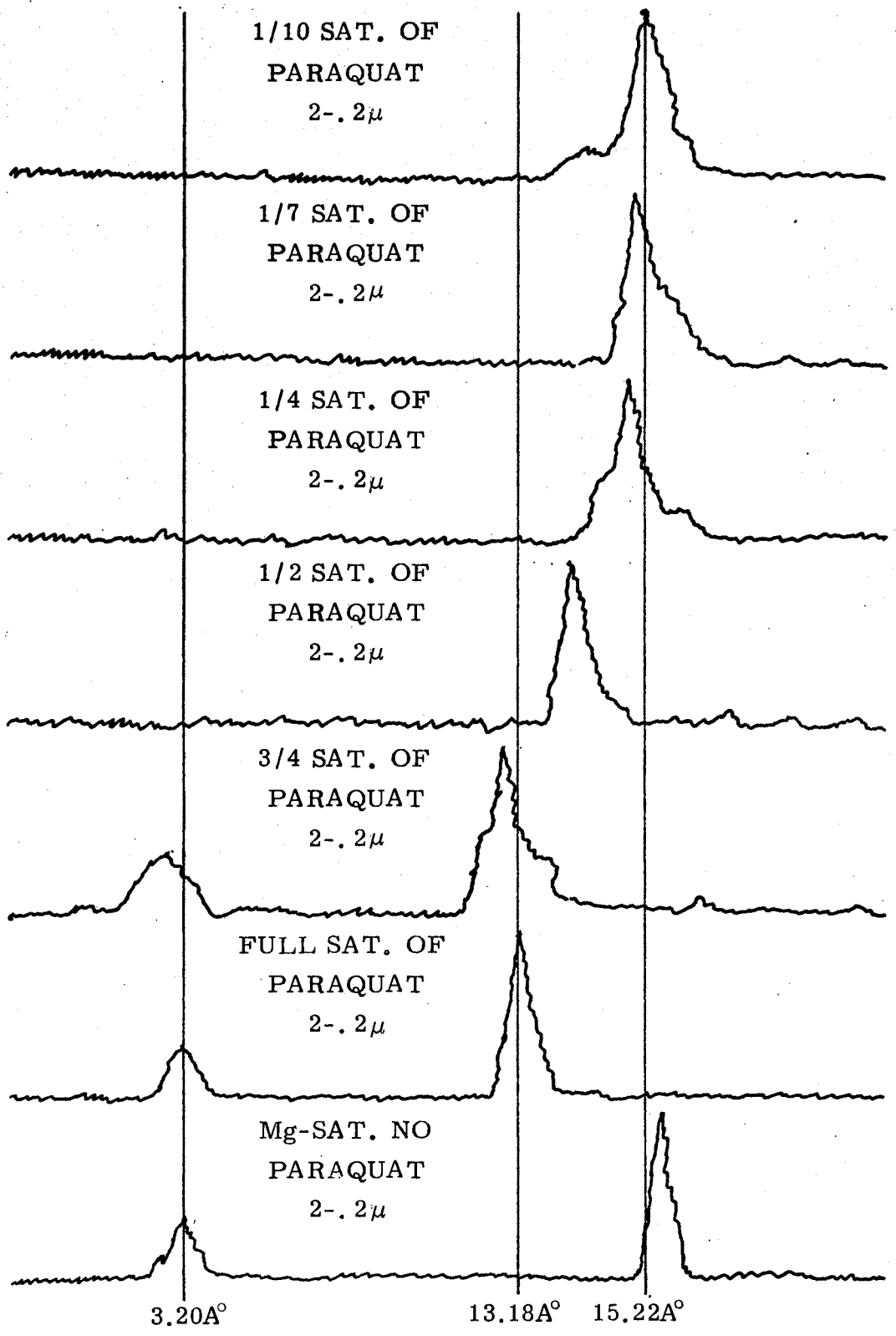


Figure 26. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Nontronite Saturated with Different Fractions of Paraquat

of nontronite from 15.49A° to 13.18A°. Fractions of 1/10, 1/7 and 1/4 of paraquat had little effect on the d-spacing of nontronite; however, the diffraction maximum decreased from 15.49A° to 14.96A°. Full and 3/4 saturations of diquat decreases the d-spacing of nontronite from 15.49A° to 13.38A°. This indicates that paraquat sorbed more organic cation in the interlayer of nontronite.

7. Nontronite 35A or 33A. The x-ray diffraction patterns of nontronite 35A or 33A are shown in Figures 27 and 28. The only difference between nontronite and nontronite 35A or 33A was that nontronite had a peak at 15.49A° when saturated with $MgC\ell_2$, while nontronite 35A or 33A had a peak at 14.96A°. D-spacing for this mineral between different fractions of diquat and paraquat was the same as nontronite.

X-ray Diffraction Pattern of Vermiculite

Vermiculite does not sorb paraquat or diquat into the interlayers as readily as montmorillonite. Therefore, the d-spacing of vermiculite did not decrease nor expand when the clay was saturated with different fractions of paraquat and diquat. Since vermiculite had a high cation exchange capacity, it therefore had a high sorption rate and x-ray diffraction results show that vermiculite increases its diffraction intensity four-fold when it is fully saturated with these organic cations. The x-ray diffraction patterns of vermiculite are shown in Figures 29 and 30. Attempts were made to remove an $A\ell$-interlayer of vermiculite and then fully saturate with paraquat (Figure 31). The results show that the 24.52A° and 12.44A° peaks were both collapsed on $A\ell$ removal and the 14.47A° peak expanded to a 14.97A° peak. This method could be used for identification of vermiculite.

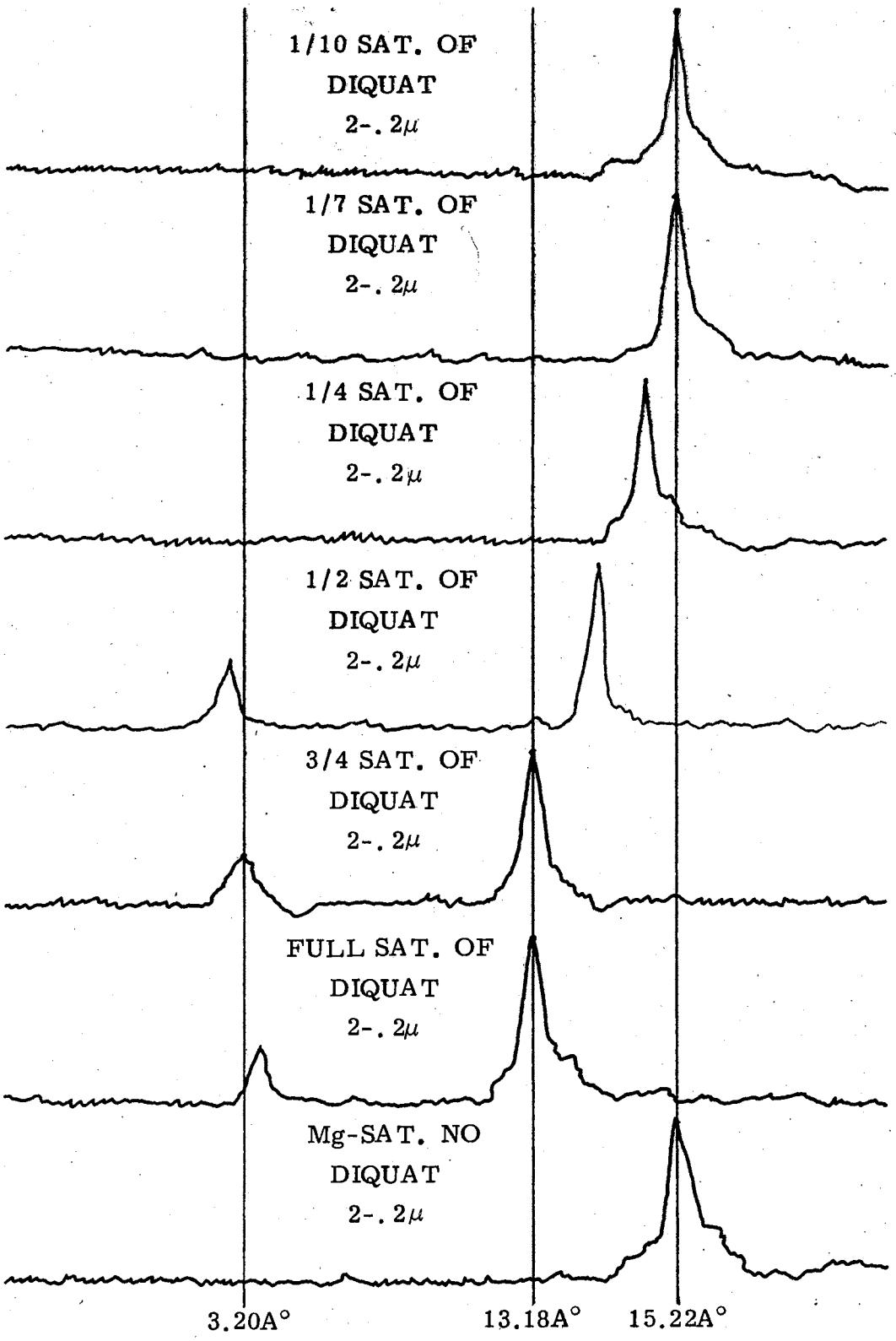


Figure 27. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Nontronite 35A or 33A Saturated with Different Fractions of Diquat

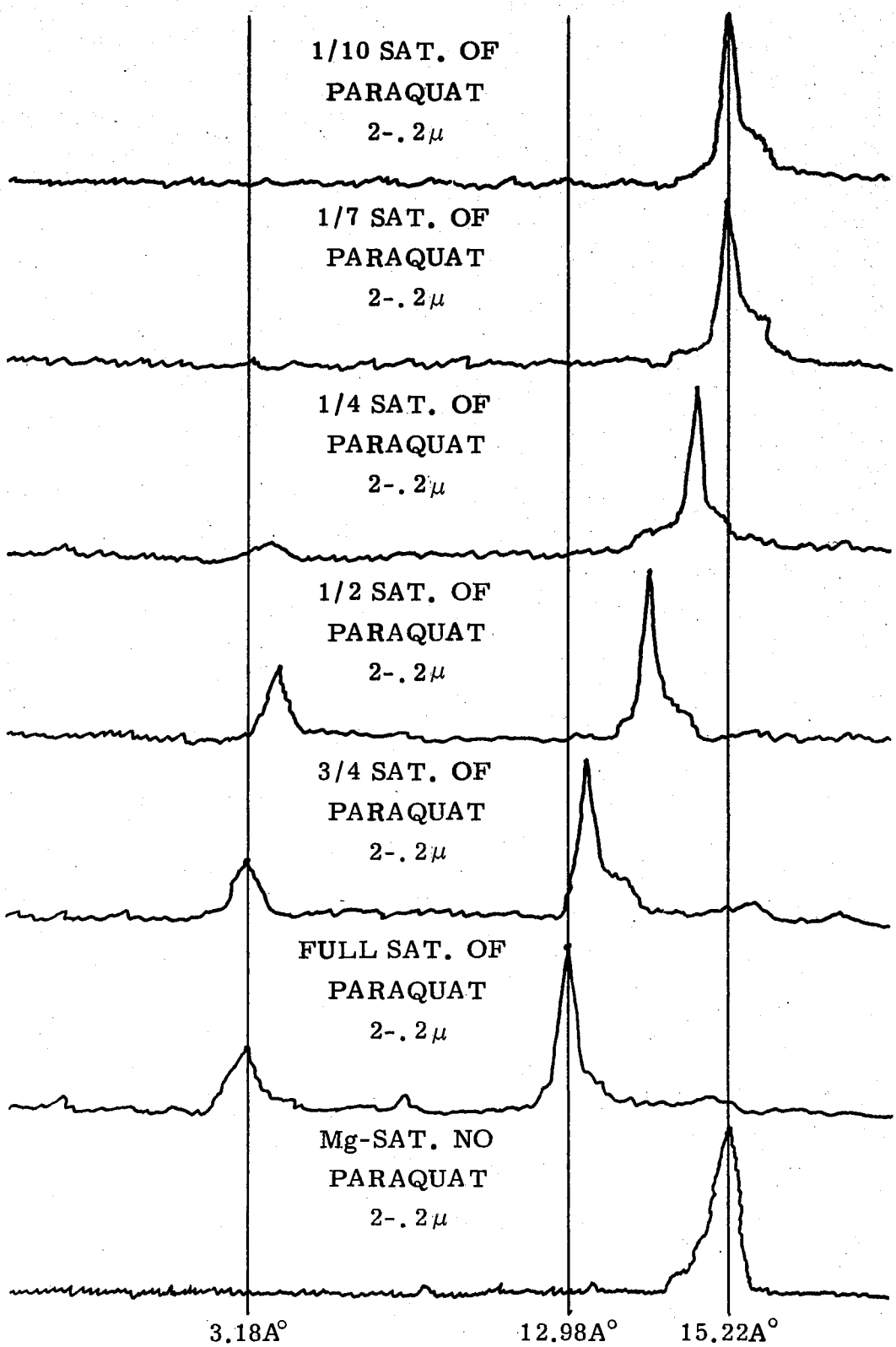


Figure 28. X-ray Diffraction Pattern of Coarse Clay (2-.2μ) of Nontronite 35A or 33A Saturated with Different Fractions of Paraquat

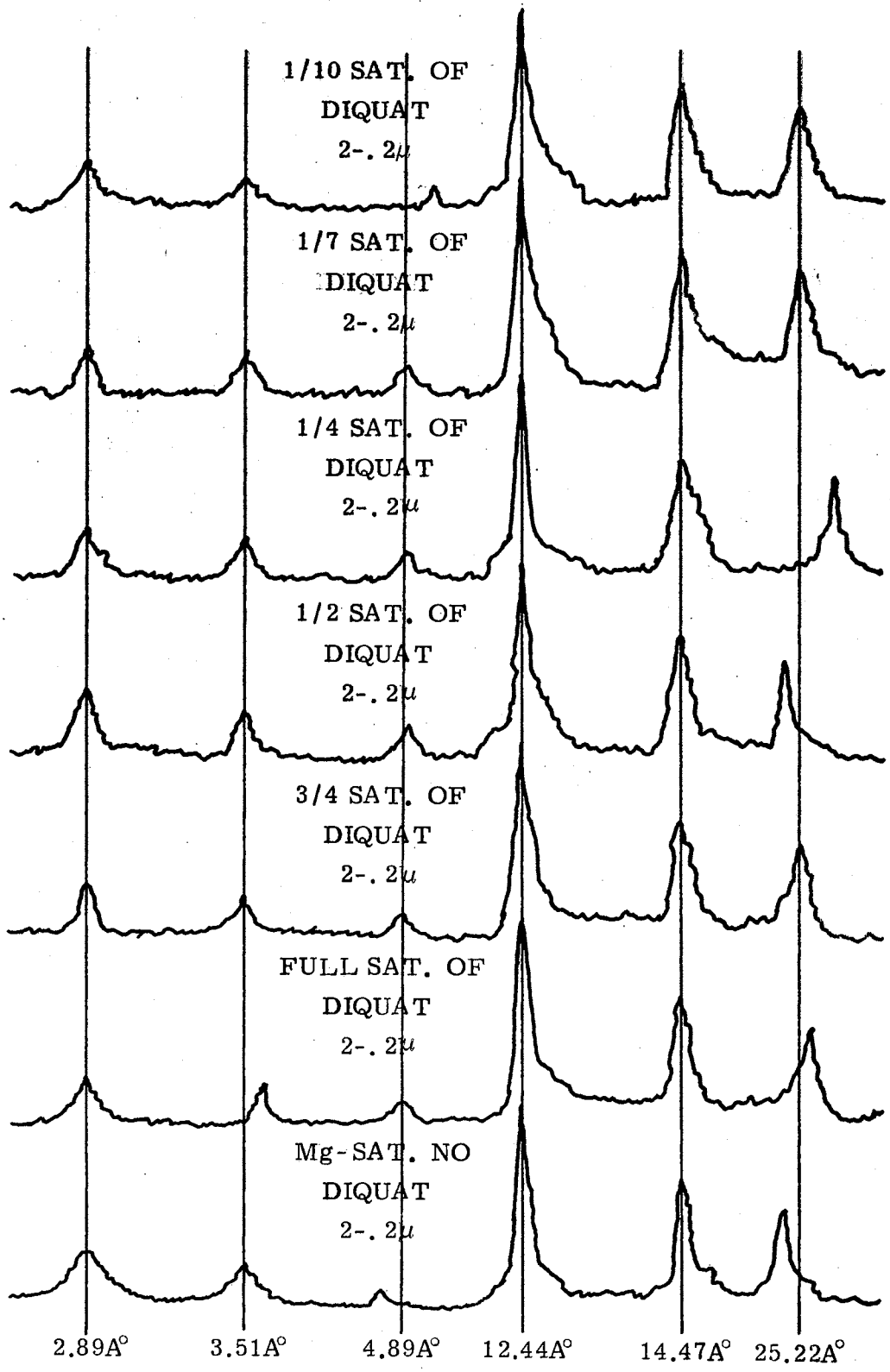


Figure 29. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Vermiculite Saturated with Different Fractions of Diquat

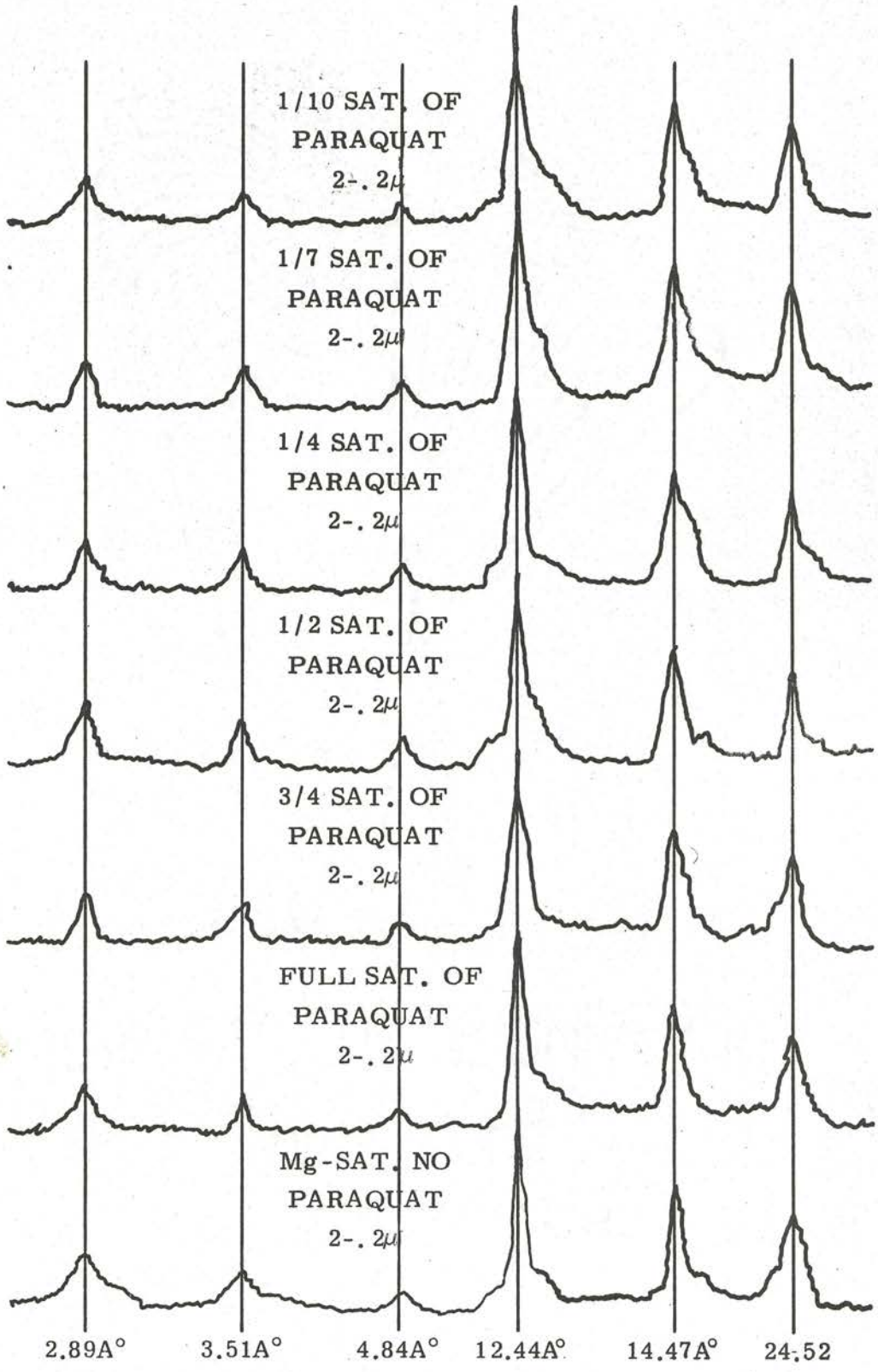


Figure 30. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Vermiculite Saturated with Different Fractions of Paraquat

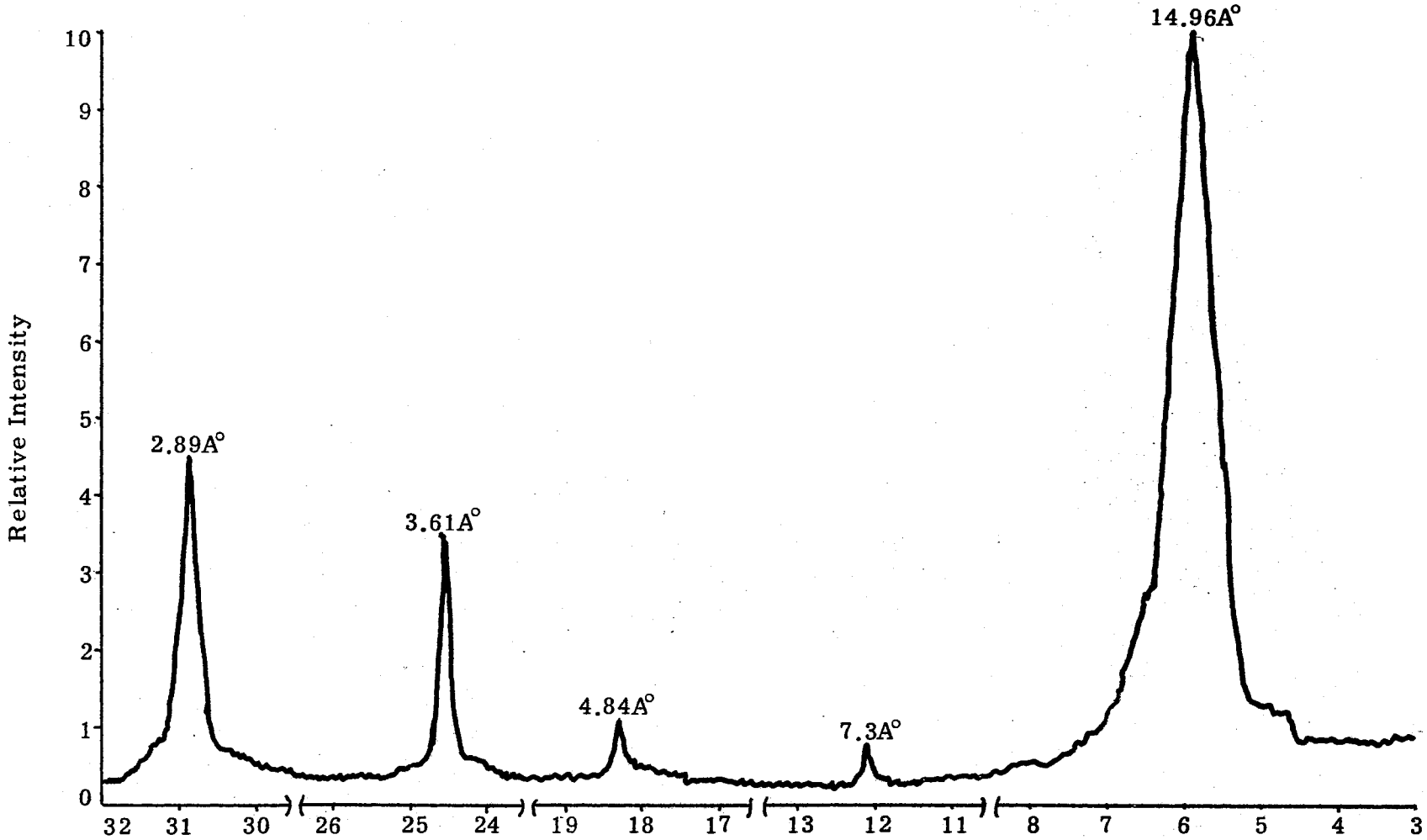


Figure 31. X-ray Diffraction Pattern of Coarse Clay (2-.2μ) of Vermiculite with Aℓ Removed and Fully Saturated with Paraquat

X-ray Diffraction Pattern of Fithian Illite

Fithian illite is described as a 2:1 nonexpandable clay mineral. The results of this study show that different fractions of paraquat and diquat had no effect on the d-spacing of Fithian illite. The x-ray diffraction patterns of Fithian illite are shown in Figures 32 and 33.

X-ray Diffraction Pattern of Georgia Kaolinite

Since kaolinite is a nonexpanding type of clay mineral, different fractions of diquat and paraquat had no effect on the d-spacing of this clay. X-ray diffraction patterns of kaolinite are shown in Figures 34 and 35.

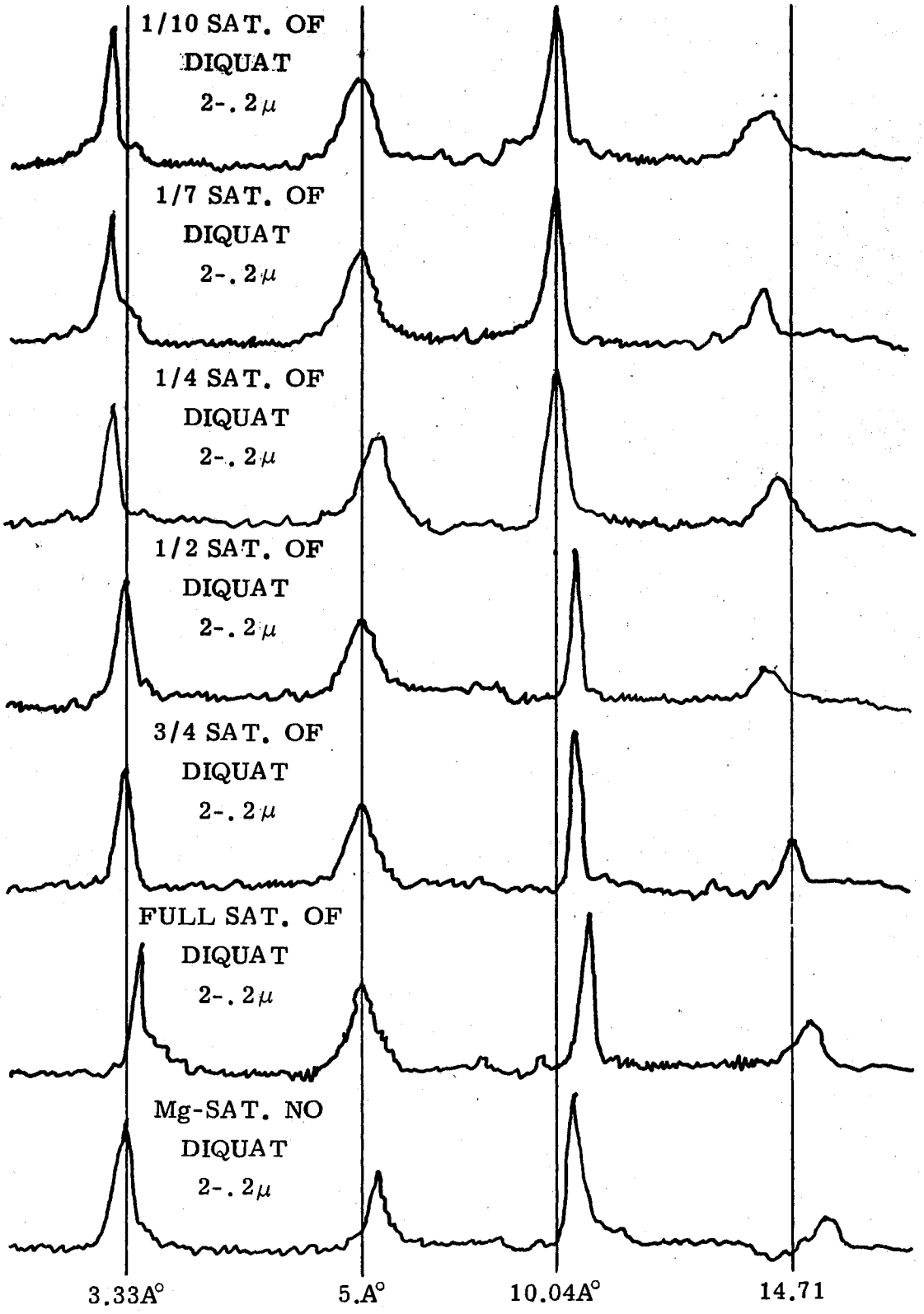


Figure 32. X-ray Diffraction Pattern of Coarse Clay (2-.2μ) of Fithian Illite Saturated with Different Fractions of Diquat

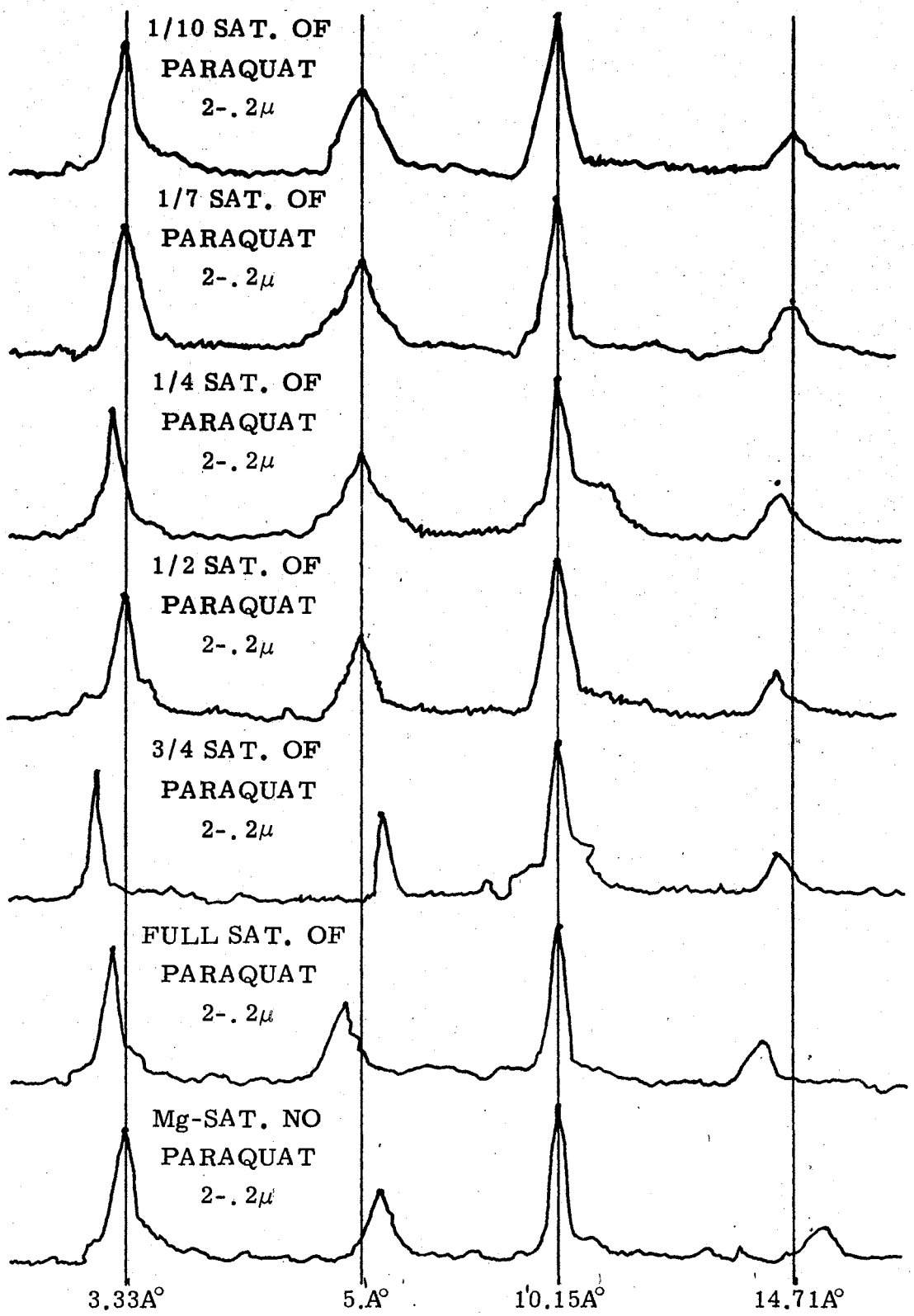


Figure 33. X-ray Diffraction Pattern of Coarse Clay (2-.2μ) of Fithian Illite Saturated with Different Fractions of Paraquat

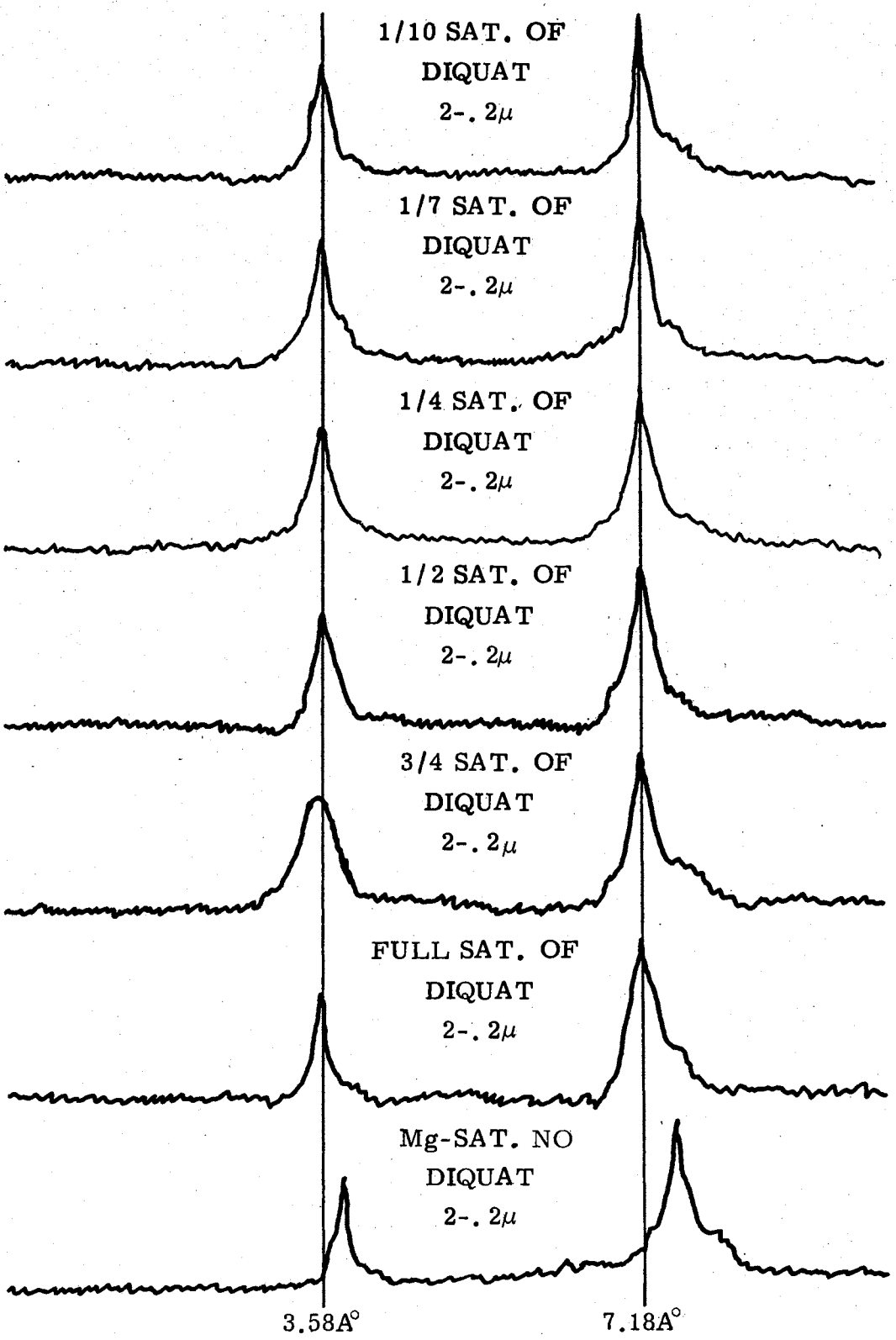


Figure 34. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Georgia Kaolinite Saturated with Different Fractions of Diquat

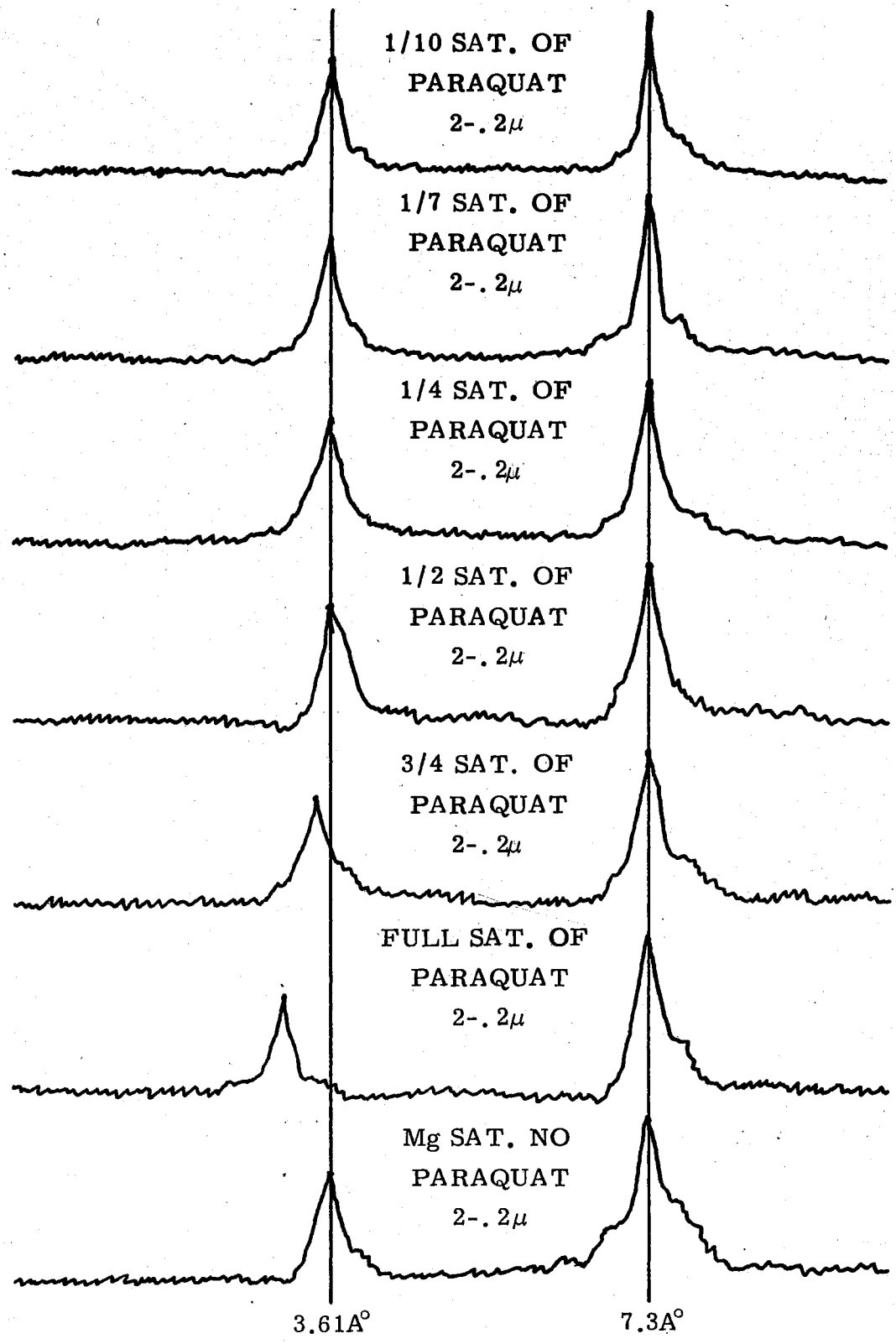


Figure 35. X-ray Diffraction Pattern of Coarse Clay (2-. 2μ) of Georgia Kaolinite Saturated with Different Fractions of Paraquat

CHAPTER V

SUMMARY AND CONCLUSIONS

The objective of this study was to determine the sorption of herbicides as a possible tool for the identification of clay minerals. Clay minerals kaolinite, illite and montmorillonite groups were used in this study. Paraquat and diquat were found to be sorbed by these clay minerals in amounts slightly less than the C. E. C. of the clays. Diquat sorption exceeds paraquat sorption in almost all clay minerals; this is probably due to the smaller size of the diquat ion, which results in less steric hindrance. The coarse fractions of clay minerals sorbed more diquat and paraquat than the fine fractions. The organic cations were probably sorbed around the edges of attapulgite, kaolinite and illite due to broken bond charges. Vermiculite and montmorillonite sorbed the organic cation within the clay structure due to isomorphic charge deficits. The x-ray diffraction results show that the montmorillonite group decreases their d-spacing by about 3A° when saturated with these cations. This method could be used for identification of the clay minerals, because the clay minerals vermiculite, montmorillonite and chlorite have a peak at 14A° or 15A° and full saturation of these minerals with diquat or paraquat would allow us to determine the montmorillonite group at 12.8A°, the vermiculite group at 14.7° and by heating the sample to 500C°, the chlorite fraction would not collapse.

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